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Pulp and Paper Mill Effluents in a Freshwater Environment

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Journal de l'office des recherches sur les pêcheries du Canada

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Pulp and Paper Mill Effluent in a Freshwater Environment[1]

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KELSO, J. R. M., C. K. MINNS, AND R. J. P. BROUZES. 1977. Pulp and paper mill effluent in a freshwater environment. J. Fish. Res. Board Can. 34: 771–775.

Background and scope are provided for joint Ontario Ministry of the Environment and Department of the Environment studies of the effect of a pulp and paper mill effluent in a freshwater ecosystem. Brief descriptions of pertinent features of the pulp and paper mill and Nipigon Bay are given as related to studies presented in this volume.

KELSO, J. R. M., C. K. MINNS, AND R. J. P. BROUZES. 1977. Pulp and paper mill effluent in a freshwater environment. J. Fish. Res. Board Can. 34: 771–775.

Cet article sert d'arrière-plan et définit la portée d'études entreprises conjointement par les ministères ontarien et fédéral de l'Environnement sur l'effet de l'effluent d'un moulin de pâges et de papier sur un écosystème d'eau douce. On y présente de brèves descriptions des caractéristiques du moulin de pâte et de papier et de la baie Nipigon pertinentes aux études contenues dans ce numéro.

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THE International Joint Commission (IJC), established in 1909 under sanction of the Boundary Waters Treaty Act, is charged, as part of its responsibilities, with conducting extensive investigations on questions arising between the Canadian and United States governments along their common frontier. Findings complete with recommendations are reported by the IJC to respective governments. Seriously concerned with the deteriorating water quality of the lower Great Lakes

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

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and with preserving the pristine nature of the upper Great Lakes, the two governments signed, April 1972, the Canada–U.S. Agreement on Great Lakes Water Quality and assigned the IJC special responsibilities and functions in overseeing its implementation. The Agreement provides a mechanism for jointly attacking the known pollution problems in the Great Lakes and identifying new problems in water quality. The concern expressed by the Governments for protecting the upper lakes was reflected in the establishment of the Upper Lakes Reference Group (ULRG), a reference group to IJC as specified in the Agreement. This group was charged with undertaking a comprehensive study of pollution problems in Lake Superior, Lake Huron, and their connecting waters and reporting their findings to IJC. It is within the ULRG framework that the research reported within this volume was undertaken.

The oligotrophic upper Great Lakes have shown little environmental change since the turn of the century (Beeton 1969) although instances of localized altered water quality have occurred. In general, the effect of local perturbations in an aquatic ecosystem depends upon the nature and behavior of the particular chemical species, the physicochemical characteristics of the receiving water, and the response and/or susceptibility of the resident biota. Because of the notable localized nature of altered water quality in the upper lakes, the following studies were designed to determine wastewater effects, in time and space, through coordinated studies on physical dispersion and chemical and biological characteristics. Although such a framework could conveniently fit the study of almost any shoreline point-source discharge to a receiving water body, a pulp and paper mill was chosen because of the presence of many such mills in the upper Great Lakes system and its recognized and potential perturbative effect on aquatic ecosystems. The requirement for increased understanding of perturbative effect resulted in this joint undertaking by the Ontario Ministry of the Environment and the Department of the Environment.

In 1973, a feasibility study was undertaken at the American Can Co. kraft mill at Marathon, Ont. (Fig. 1). Generally, results of these experiments served primarily to redirect experimental approaches, especially methods to follow plume centerline paths, and led to the final selection of Nipigon Bay as a more appropriate study site. Research reported herein, therefore, results from studies jointly undertaken in Nipigon Bay, Lake Superior, during summer 1974. Results of that research are chronologically presented in this volume in the following categories of convenience:

i) Effluent dispersion and plume processes
ii) Ecosystem response and features not necessarily confined to discrete plumes
iii) Testing of effluent effects upon biota
iv) Plume oriented biological studies.

The Red Rock Mill

The Domtar Red Rock mill (Fig. 2) is a dual product mill with an approximate annual production of 61,000 t of newsprint and 203,000 t of kraft linerboard. The linerboard is used primarily in the manufacture of corrugated boxes. The mill began production as an unbleached sulphate (kraft) pulp mill in 1945. In 1948, a groundwood pulp mill was added to the operation. In 1954, a paper machine for the production of kraft linerboard was added and the original paper machine was converted to the production of newsprint from groundwood. A series of process changes for environmental improvement of the effluent has occurred during the mill's recent history. Prior to studies reported here, log drives were phased out, a causticising plant and lime kiln were installed to reduce losses of calcium carbonate, and the black liquor handling system

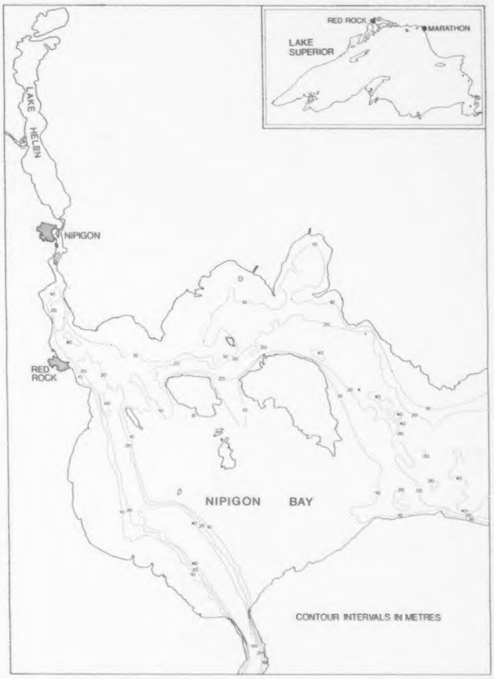

FIG. 1. Lake Superior showing location of Marathon and Red Rock including Nipigon Bay.

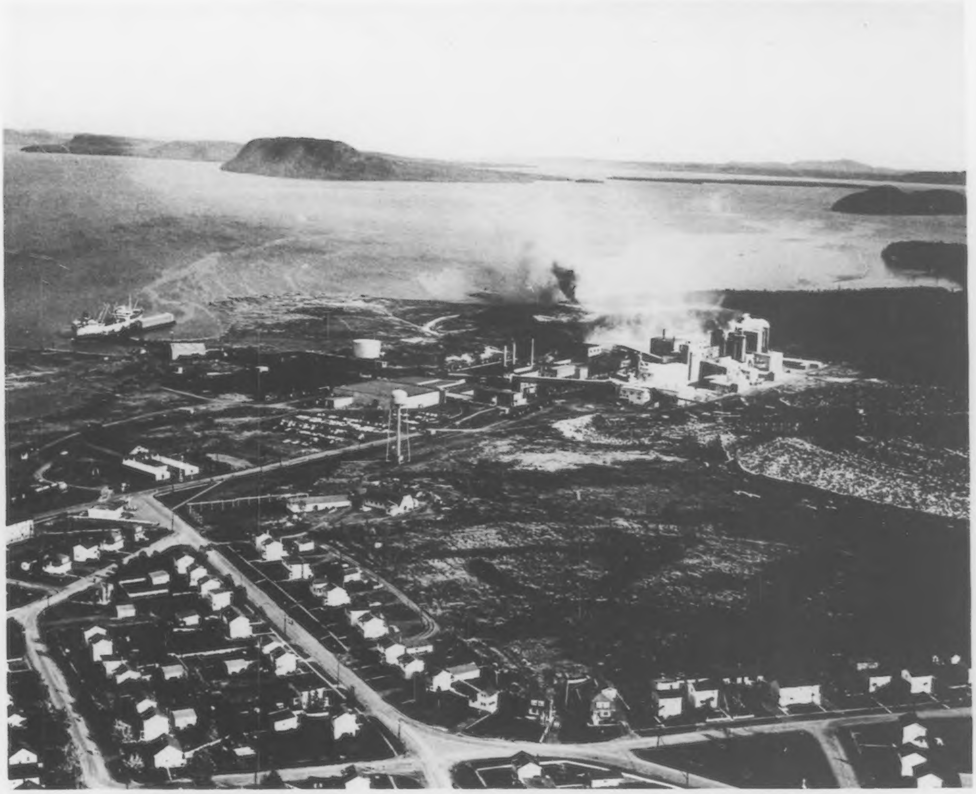

FIG. 2. Aerial photograph of the Domtar Red Rock mill, Nipigon Bay.

was tightened. Perhaps one of the most important modifications was the installation of an external treatment clarifier in 1973 for removal of fiber from wastewater. Following these studies, a condensate steam stripper was installed to eliminate volatile (primarily sulphurous) odorous and toxic materials.

Until 1973, most logs destined for the mill were transported by local waterways, primarily the Nipigon River (Fig. 1). Jack pine and black spruce were floated to storage areas in Lake Helen or Nipigon Bay. At the mill, logs were withdrawn from the water, cut to lengths and introduced to the pulping process. Today, wood arrives by truck or train either as logs or chips.

The two most important North American pulping procedures, chemical and mechanical, are both used at the Red Rock mill. Pulping of wood can be carried out by four methods: chemical, semi-chemical, chemichemical and mechanical with the order representing increasing yields of pulp (from about 42 to 95%) from available cellulose fiber. Kraft pulping involves the use of sodium hydroxide and sodium sulphide which dissolves lignin from the wood in such a way that the cellulose fibers can be separated, i.e. pulped. Groundwood pulp is produced by mechanical separation of fibers by friction against stones (for further details of both processes see Tomlinson 1968). At the Red Rock mill, groundwood pulp is currently used only in the newsprint operation where it is combined with approximately 20% of semibleached pulp.

Residual amounts of lignin in the pulp can be removed by chlorination, thereby increasing paper brightness. The reaction products include carbon dioxide, water, and a variety of cleaved and uncleaved chlorinated and unchlorinated aromatics. Resin acids, fatty acids, and terpenes which are also present in the effluent appear to form the primary known toxic constituents.

Although the Red Rock wastewaters are discharged through one canal entering Nipigon Bay (Polak and Palmer 1977) three mill process streams converge into this one discharge. An "uncontaminated" stream (approximately 10 m^3/min) of machinery coolant water joins a low suspended solids stream (13.7–18.2 m^3/min) containing materials from paper machines, kiln causticizing area, bleach plant, etc. near the mill. The largest stream (40.9–50.0 m^3/min) comes from the clarifiers which remove wood fiber from wastewaters of paper machines, wood room, groundwood mill, and the kraft digestor/washer screen area. Additionally, the town of Red Rock discharges sewage waste (1.6 m^3/min) via the same discharge canal. Process waters are defoamed using commercial defoaming agents and wastewaters pass under a series of foam barriers from which they flow into Nipigon Bay.

Nipigon Bay

Nipigon Bay, in the northernmost corner of Lake Superior (Fig. 1), is fed primarily by the Nipigon River which enters the bay at the townsite of Nipigon, the major settlement of the watershed. The river has delivered, over the period 1950 to 1968, a mean annual flow of 365.3 m^3/s. This anual mean flow has varied by a factor of 2 (245.2 m^3/s in 1973 and 495.5 m^3/s in 1969). Flows during the months of June, July, and August, the timing of this study, are generally far above the annual mean. In 1974, mean annual flow was 387.9 m^3/s and monthly means were 563.5, 566.3, and 498.3 m^3/s for June, July, and August, respectively.

The shores of Nipigon Bay are girdled by ranges of high, imposing rocky hills rising up to 200 m above the lake. Nipigon Bay itself extends about 16 km south and 40 km east from the entry of the Nipigon River. Two primary channels exist in the bay. The channel running south cuts between Five Mile Point, just south of the Domtar mill, and Burnt Island. The other channel parallels the northern shore of the bay. These channels tend to govern main directions of water flow (Polak and Palmer 1977).

These waters once supported a wide variety of fish species including lake trout, walleye, whitefish, and lake herring; however, the area has never attracted a major tourist industry (German 1966). These once abundant fish stocks are now limited or rare. A precipitous decline in walleye, the last of the most sought-after commercial stocks, was observed during 1958–67 (Ryder 1968). Commercial fishing catches have periodically been rejected for sale because of objectionable taste and odor. Many studies presented herein address, directly or indirectly, this aspect. No definitive answer was forthcoming, however, either as to responsible compounds or mode of action.

Red Rock Studies

Contributions provided herein only partly achieved an inherent goal; namely, to model the fate and effect of a perturbative process affecting a nearshore upper Great Lakes environment. Conversely, studies neither lacked cohesion nor failed to achieve their original stated intents. Pervasive problems became apparent on site in 1974 and became clearer when chemists began tasks of compound identification, modellers attempted to describe the processes, and biologists sought factors governing observed responses. The lack of hydrologic understanding of Nipigon Bay was likely the largest obstacle, and Brownlee and Strachan (1977), Brownlee et al. (1977), Sandilands (1977), VanderWal (1977), and Rokosh et al. (1977) had to infer certain behavior patterns of water masses in developing an understanding of broad based chemical, sediment, benthic macroinvertebrate or bacterial community alterations. Plume oriented studies, however, fared considerably better as dye, drogues, and current meters provided adequate data for inspecting the tendencies in dominant localized alterations.

Plume analysis (Minns 1977; Polak and Palmer 1977) indicated that an area of approximately 1.5 km^2 was exposed to concentrations of effluent greater than 1%. Only a few percent of that loss occurring along the plume centerline trajectory was accounted for by processes other than dilution (Johnson 1977). Sandilands (1977) found generally elevated levels of organic matter near the outfall. It was this area which likely contributed to depressed macroinvertebrate communities (VanderWal 1977) and to the proposed resuspension of sedimented particulate material (Minns 1977). The area of effect imposed by the altered water quality appears plastic, however, in that the area influenced varies with the factor examined. Proceeding from most to least sensitive in biotic communities the following general sensitivity pattern develops: bacteria (Rokosh et al. 1977), benthic macroinvertebrates (VanderWal 1977), phytoplankton and periphyton (Moore and Love 1977), zooplankton (Cooley 1977), and fish (Kelso 1977; Whittle and Flood 1977). Although the areas affected coincide with the distribution of persistent organic contaminants (Brownlee and Strachan 1977) and areas influenced only by high effluent concentration, the ties between contamination and effect were not always direct. Nevertheless the most sensitive indicator appears to be bacteria while the least sensitive appears to be fish.

In general, severe ecosystem disruption, evidenced by depauperation or severe alteration in function, was restricted to an area no greater than 0.5 km^2 near the outfall. Progressive recovery occurred beyond this area. Persistence of organic compounds, e.g. dehydroabietic acid, although not directly implicated in taste and odor problems in fish, reflected the potential influence of contaminants, should their effect be either sublethal or impart undesirable taste and odor to desirable fish stocks. Combined with the fact that not all effluent components were toxic, it appears that certain groups of organic material, natural or residual, may act in concert with substances injected directly into the wastewater and thus augment conditions.

Apparent lack of response by benthic macroinvertebrates (VanderWal 1977) following several years of suspended solid removal indicates removal of problem-causing organic compounds as an immediate abatement procedure. The local alteration in community structure further indicates that, once taste and odor-creating substances are eliminated or reduced, rehabilitation of depleted desirable fish stocks is warranted.

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We, the Department of the Environment and the Ministry of the Environment, wish to thank the Domtar Packaging Company Limited for their unstinting aid throughout this study. In particular, we thank Dr G. H. Tomlinson, Dr W. H. Cook, S. S. Hessian, A. S. Kadzielawa, and R. Dupuis of Domtar.

Paul McDermott, Water Quality Branch, Inland Waters Directorate, spent many hours performing on-site water quality measurements. Many analyses of samples were performed by Water Quality Branch personnel in Burlington.

A number of persons and agencies within the Department of the Environment made the field work possible: R. Collins, W. Hyatt, G. Dunlop, C. Charlton, Great Lakes Biolimnology Laboratory; G. Koteles, B. Timmins, and their co-workers in Technical Operations of Inland Waters Directorate; Marine Sciences Directorate who provided launches and the Port Dauphine and M. Head, Marine Sciences Directorate, who helped in many ways.

BEETON, A. M. 1969. Changes in the environment and biota of the Great Lakes, p. 150–187. *In* Eutrophication: causes, consequences, correctives. Nat. Acad. Sci. Wash. D.C.

BROWNLEE, B., AND W. M. J. STRACHAN. 1977. Distribution of some organic compounds in the receiving waters of a kraft pulp and paper mill. J. Fish. Res. Board Can. 34. (This issue)

BROWNLEE, B., M. E. FOX, W. M. J. STRACHAN, AND S. R. JOSHI. 1977. Distribution of dehydroabietic acid in sediments adjacent to a kraft pulp and paper mill. J. Fish. Res. Board Can. 34. (This issue)

COOLEY, J. M. 1977. Filtering rate performance of *Daphnia retrocurva* in pulp mill effluent. J. Fish. Res. Board Can. 34. (This issue)

GERMAN, M. L. 1966. Preliminary report of the biological survey of Nipigon Bay, Lake Superior. Ont. Wat. Res. Comm. Rep. 19 p.

JOHNSON, M. G. 1977. Caloric changes along pulp and paper mill effluent plume. J. Fish. Res. Board Can. 34. (This issue)

KELSO, J. R. M. 1977. Density, distribution, and movement of Nipigon Bay fishes in relation to a pulp and paper mill effluent. J. Fish. Res. Board Can. 34. (This issue)

MINNS, C. K. 1977. Analysis of a pulp and paper mill effluent plume. J. Fish. Res. Board Can. 34. (This issue)

MOORE, J. E., AND R. J. LOVE. 1977. Effect of a pulp and paper mill effluent on the productivity of periphyton and phytoplankton. J. Fish. Res. Board Can. 34. (This issue)

POLAK, J., AND M. D. PALMER. 1977. Concentration pattern of chemical constituents in a paper mill's effluent plume: dynamics and model. J. Fish. Res. Board Can. 34. (This issue)

ROKOSH, D. A., S. S. RAO, AND A. A. JURKOVIC. 1977. Extent of effluent influence on lake water determined by bacterial population distributions. J. Fish. Res. Board Can. 34. (This issue)

RYDER, R. A. 1968. Dynamics and exploitation of mature walleyes, *Stizostedion vitreum vitreum*, in the Nipigon Bay region of Lake Superior. J. Fish. Res. Board Can. 25: 1347–1376.

SANDILANDS, R. G. 1977. Effect of pulp mill effluent on the sediments of western Nipigon Bay, Lake Superior. J. Fish. Res. Board Can. 34. (This issue)

TOMLINSON, G. H. 1968. Pulp, *In* Encyclopedia of chemical technology. Vol. 16, 2nd ed. J. Wiley and Sons, Inc., New York, N.Y.

VANDER WAL, J. 1977. Relation between Nipigon Bay benthic macroinvertebrates and selected aspects of their habitat. J. Fish. Res. Board Can. 34 (This issue)

WHITTLE, D. M., AND K. W. FLOOD. 1977. Assessment of the acute toxicity, growth impairment, and flesh tainting potential of a bleached kraft mill effluent on rainbow trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 34. (This issue)

Analysis of a Pulp and Paper Mill Effluent Plume[1]

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MINNS, C. K. 1977. Analysis of a pulp and paper mill effluent plume. J. Fish. Res. Board Can. 34: 776–783.

Several chemical surveys of a pulp and paper mill effluent plume in Nipigon Bay, Lake Superior, are analyzed to determine the average area and volume contained by a range of isoconcentration boundaries. Sodium, dissolved organic carbon, particulate organic carbon, and particulate organic nitrogen are the chemical variables used to examine changes occurring in the plume. Data are analyzed from three sampling regimes: (1) dye-slug tracking which allows interpretation of time-related processes, (2) surface surveys which indicate the areal extent of the plume, and (3) vertical profile surveys which indicate the degree of depth penetration for effluent components.

Dilution dominates in the plume, though the nonconservative substances undergo significant changes. The plume area enclosed in a contour of 1% effluent is approximately 1.5 km². Mass balance calculations indicate exchanges occurring between the plume and the old fiber beds in the vicinity of the effluent outfall.

MINNS, C. K. 1977. Analysis of a pulp and paper mill effluent plume. J. Fish. Res. Board Can. 34: 776–783.

Nous analysons plusieurs relevés chimiques de la zone superficielle de l'effluent d'une usine de pâte et de papier dans la baie de Nipigon, lac Supérieur, en vue de déterminer la superficie et le volume moyens contenus dans une gamme de limites de même concentration. Nous nous sommes servis de quatre paramètres chimiques, y compris l'ion conservateur sodium, pour étudier les changements qui se produisent dans la zone superficielle. Nous analysons les données de trois régimes d'échantillonnage : (1) dépistage de piécettes de colorant permettant l'interprétation des processus dépendant du temps, (2) relevés de la surface indiquant l'étendue de la zone superficielle et (3) relevés de profils verticaux indiquant le degré de pénétration en profondeur des composantes de l'effluent.

La dilution domine dans la zone superficielle, bien que des substances non conservatrices subissent d'importants changements. La superficie de la zone superficielle comprise dans le contour d'une concentration de 1% d'effluent est d'environ 1.5 km². Les calculs de balance de masse indiquent qu'il se produit des échanges entre la zone superficielle et les vieux tapis de fibres dans le voisinage de l'exutoire de l'effluent.

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STUDIES of the dispersion of industrial effluents released into aquatic ecosystems are an important component of assessing the overall impact in those ecosystems. While there have been numerous analyses of plumes, the majority have been concerned with the dispersion of heated cooling water released by fossil-fuel and nuclear power plants. This study presents an analysis of the plume resulting from the discharge of the Red Rock pulps and paper mill effluent into Nipigon Bay, Lake Superior, using four chemical parameters.

The primary purpose of this study was to obtain a single "picture" of the area and volume of the plume bounded by various dilutions of effluent. The second intention was to measure different chemical variables and to assess the implications of any differences regarding processes occurring in the plume. The final purpose was to provide other scientists measuring ecosystem response to various dilutions of effluent with a means of generalizing observations, with a view to assessing the impact of the plume on ecosystem components such as plankton and fish in Nipigon Bay.

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

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Studies on cooling water plumes (Ashbury and Frigo 1971; Elliott and Harkness 1972) have shown that discharge rate is the primary factor determining the area and volume development of a plume, while auxiliary factors such as wind stress and currents determine the exact spatial configuration of the plumes. Since discharge exhibited only minimal variance among the sampling days in the study period, the analytical approach adopted here attempts to explain only the average properties of the plume.

Since the sampling regimes encompassed a large area (approximately a 2-km radius of the outfall) and since concurrent hydrodynamic observations in Nipigon Bay are highly localized, an empirical descriptive analysis of data is utilized rather than any a priori 2- or 3-dimensional dispersion model.

Methods

Four chemical variables — sodium, dissolved organic carbon, particulate organic carbon, and particulate organic nitrogen — were determined in three separate sampling regimes. Chemical analyses were performed by the Water Quality Branch at the Canada Centre for Inland Waters, using methods described in the Analytical Methods Manual (Inland Waters Directorate 1972). Samples were prepared for analysis in the field, usually on the sample collection day. The choice of chemical variables provided a number of useful contrasts. Sodium (Na) has been generally shown to be a conservative element and thus can provide information about advection and mixing processes in the aquatic environment. Also, large quantities of sodium sulphate (Na_2SO_4) are used in the mill operation. Dissolved organic carbon (DOC) is a useful indicator of the many organic compounds released into the water during the mill processing of wood fiber (Fox 1976). Particulate organic carbon (POC) and particulate organic nitrogen (PON) are useful indicators of pulp and paper waste particulate release into the environment. POC and PON also provide a useful contrast with respect to the Na and DOC regarding biological production and sedimentation of particulate matter.

The first sampling regime was concerned with the time-related movement and dilution of the effluent along a centerline trajectory in the plume. On eight occasions, a slug of the conservative dye, Rhodamine WT, was introduced at or near the effluent discharge. At time intervals thereafter the center (highest concentration of dye in the top 1–1.5 m of water) of the dye cloud was relocated, the position was fixed, and water samples were taken. Usually the dye-cloud center was then recharged with dye to make further relocations simpler. The location of the dye-cloud was determined using a continuous-flow fluorometer in a boat in conjunction with visual observations from a light aircraft. Dye-slug experiments generally lasted 6–8 h, depending on weather conditions and how early in the daylight period the experiment began.

On all days when dye-slug experiments were performed, the other sampling regimes were implemented. In the second sampling regime, a crew visited a series of fixed stations (Fig. 1) in a small boat and obtained a series of samples at different depths for analysis. The samples allowed examination of vertical variations of concentration. At the same time, in the third sampling regime, a boat cruised a set of fixed lines at constant speed and frequent samples (every few minutes) were obtained by sampling from a continuous flow of water pumped from just below the water surface in front of the boat. The full set of survey lines is shown in Fig. 1 though only a subset (8–12 lines) was surveyed on any particular day. The lines most often used were those that terminated at fixed vertical sampling stations. Both the vertical and surface surveys usually took 2½–3 h.

The method of analysis used here assumes that data from each sampling day provide a synoptic picture of the plume but because of the minimal variation observed in discharge rate, the data are pooled across days in all analyses. As is commonly done in plume analysis, the concentrations for each chemical variable are converted to a relative concentration lying between 1 (the effluent) and 0 (the background level) using the equation:

$$(1) \quad C_r = (C_a - C_b)/(C_e - C_b)$$

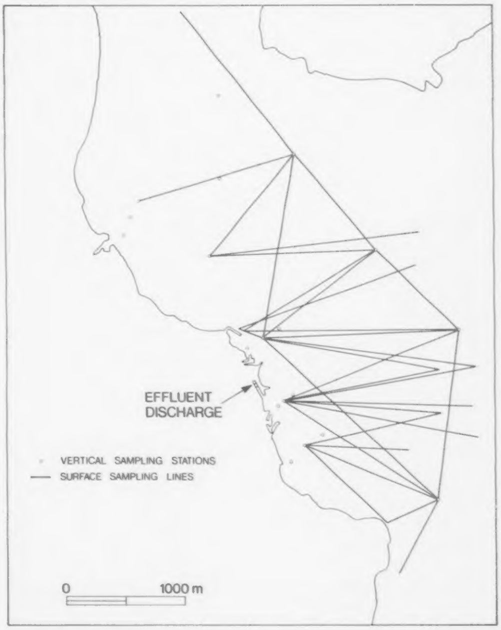
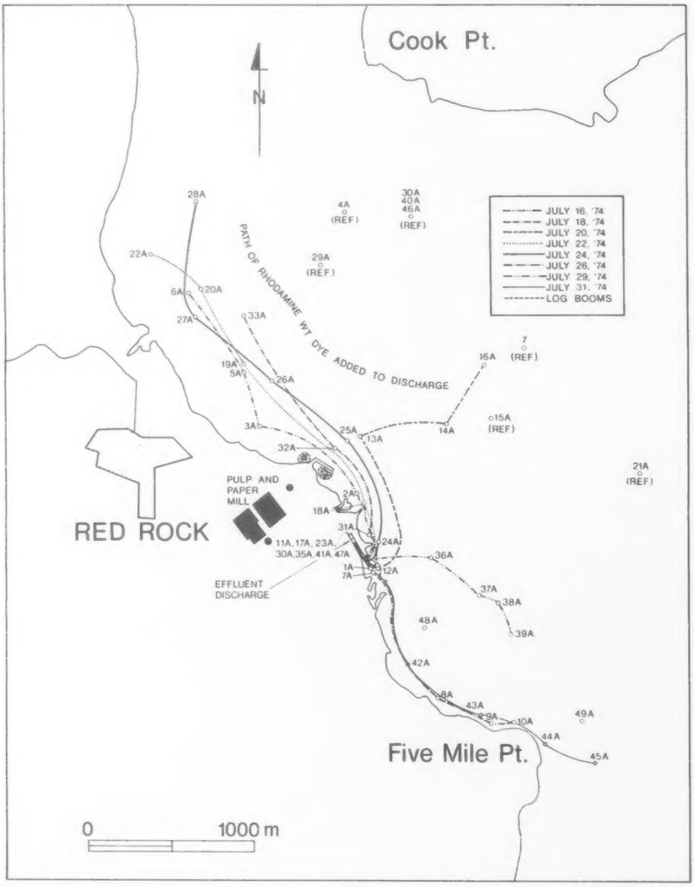


FIG. 1. Locations of vertical sampling stations and surface sampling lines in the vicinity of the Red Rock pulp and paper plant, Nipigon Bay.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JULY 16, '74
JULY 18, '74
JULY 20, '74
JULY 22, '74
JULY 24, '74
JULY 26, '74
JULY 29, '74
JULY 31, '74
LOG BOOMS
PATH OF RHODAMINE WT DYE ADDED TO DISCHARGE
22A
29A (REF)
6A
20A
27A
33A
7 (REF)
16A
19A
5A
26A
3A
25A
13A
14A
15A (REF)
32A
21A (REF)
PULP AND PAPER MILL
2A
18A
RED ROCK
31A
11A, 17A, 23A, 30A, 35A, 41A, 47A
24A
36A
1A
7A
12A
EFFLUENT DISCHARGE
37A
38A
48A
39A
42A
8A
43A
9A
10A
49A
44A
Five Mile Pt.
45A
0
1000 m

FIG. 2. Trajectories of dye-slug introduced at or near the outfall on several days in July 1974.

where C_e = effluent concentration
C_b = background concentration
C_a = concentration to be converted
C_r = relative concentration

This conversion is equivalent to assuming the substances in the effluent are diluted in a substance-free medium. Background concentrations (C_b) for each day are defined as the mean of the five least values in the surface survey and the five least values in the vertical survey. There is little difference between the two sets of values in the majority of cases and generally values came from stations that are the furthest removed from the effluent outfall. The effluent and background concentration data are summarized along with discharge data in Table 1. Each day's data are converted separately and zero values excluded. Each chemical variable is treated separately throughout the analyses presented here.

Results

Data from the dye-slug experiments provide information on the time related dilution of relative concentration in the plume's centerline trajectory. The trajectories for each day are shown in Fig. 2. The plumes usually ran alongshore as the wind generally ran parallel to the shoreline. Two ran southwards very close to the shore while the northward four tended to move slightly offshore. On the two days when the trajectory was offshore, the wind was undergoing a transition between NW and SE.

Regressions between relative concentration (C_r) and time (T) using the equation:

(2) $\log_e C_r = a + b \log_e T$ (h)

where a and b are fitted coefficients

TABLE 1. Data on effluent (C_e) and background (C_b) chemistry and discharge for the pulp mill during July 1974.

Variable	Units	Source	Mean	Range
Sodium (Na)	mg/ℓ	C_e	105.9	160.0–48.0
	mg/ℓ	C_b	1.4	1.5–1.3
Dissolved organic carbon	mg/ℓ	C_e	110.3	182.0–52.0
(DOC)	mg/ℓ	C_b	4.7	5.2–4.2
Particulate organic carbon	mg/ℓ	C_e	21.637	39.000–14.690
(POC)	mg/ℓ	C_b	0.206	0.242–0.173
Particulate organic nitrogen	mg/ℓ	C_e	0.460	0.637–0.273
(PON)	mg/ℓ	C_b	0.025	0.035–0.014
Discharge[a]	m^3/min		65.29	71.12–54.79

[a] Based on plant operating records.

TABLE 2. Results of regression analyses[a] of relative concentration of variables versus time along the centerline trajectory.

Variable	# Values	Intercept 'a'	Slope 'b'	Regression F-value	r
Na	35	−0.138	−1.986	115.57[b]	0.882
DOC	34	−0.098	−1.827	128.59[b]	0.895
POC	35	−0.274	−1.824	108.21[b] 4	0.875
PON	35	−0.215	−1.282	93.24[b]	0.859

[a] Using equation (2) in text.
[b] Significant at $P = 0.005$.

give a good fit (Table 2). Na, DOC, and POC follow a nearly inverse-square time-dilution, while PON follows a nearly simple inverse time-dilution. Further, in the plume trajectories, time and distance travelled from the outfall are closely related:

$$(3) \quad \log_e \text{Distance (km)} = -1.488 + 1.050 \log_e \text{Time (h)} \quad (r = 0.882)$$

The slope (1.050) is not significantly different from 1; thus the exponential of the intercept (−1.488) approximates an average velocity of 0.226 km/h which is virtually constant along the trajectories.

For analysis of the surface area development of the plume versus relative concentration, the surface survey data were plotted for each day and each variable, and contour lines were drawn by hand. Two examples of surface sodium plumes along with the trajectories for those days are shown in Fig. 3. It is worth noting here that while the surface surveys took only 2 or 3 h compared with the 6–8 h for the trajectory measurements, the values obtained by the two methods were always remarkably consistent spatially, indicating a reasonable degree of stability in the plume configuration within any particular day. The areas within each contour were determined by weighing cutouts of the contours. Plots of area versus relative concentrations are shown in Fig. 4, along with the logarithmic regression equations. Only slight differences in areal development are discernible for the four chemical variables.

In plume analysis, it is common to assume that the travel-time from the source to any point on a isoconcentration line in the plume is the same as that along the centerline trajectory (Policastro 1972). Thus the time–concentration dilution equations (equation 2, Table 2) can be substituted into the concentration area equations (Fig. 4) to give areal development as a function of time (Fig. 5). PON exhibits an areal development with time less than that for Na while POC and DOC are initially lower than Na but eventually overtake that of sodium. This analysis neglects any changes that may be occurring in the vertical plane.

Most vertical profiles did not include surface measurements; samples were normally taken at 1, 3, 5, 7, and 9 m and occasionally at 0.5 and 10 m, or as water depth allowed. Thus, the vertical surveys could not be related directly to surface data. However, it was found that values obtained at any particular depth belonged to a common frequency distribution, and analysis indicated that in general the percentage cumulative frequency distribution could be described by an equation involving relative concentration and

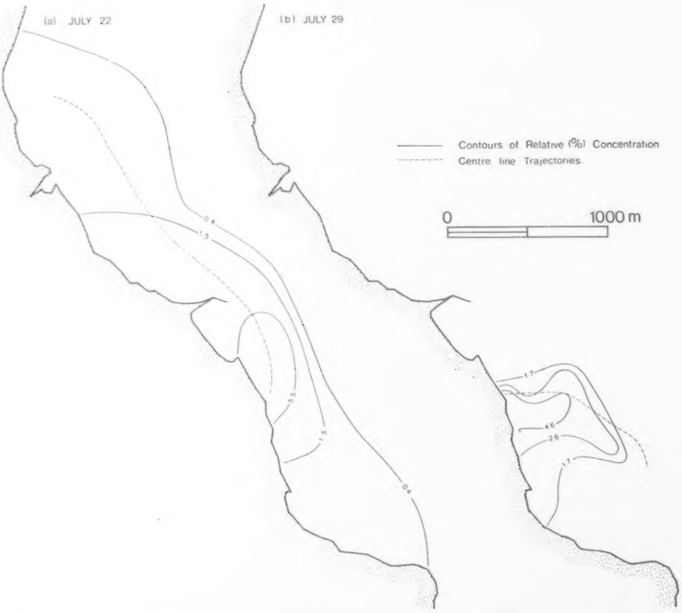

FIG. 3. Surface relative concentration contours for sodium on 2 days.

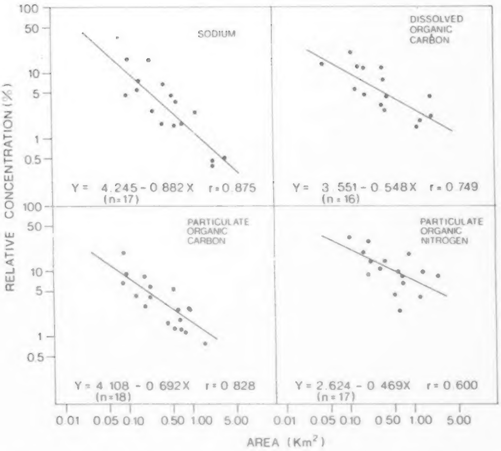

FIG. 4. Relative concentration of chemical variables versus isoline areal development (km^2) for the effluent plume. (in the equations, $Y = \log_e C_r$ and $X = \log_e$Area).

depth of the form:

$$(4) \quad Y = a + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4$$

where $Y = \log_e$ relative concentration
X_1 = depth in metres
$X_2 = \log_e (P/(1\text{-}P))$
P = percentage of samples at depth X_1 with a relative concentration less than or equal to $\exp(Y)$.
$X_3 = \log_e(\text{Depth} + 1)$
$X_4 = X_2$ times X_3
a, b_1, b_2, b_3, and b_4 are fitted coefficients.

Surface data were combined with the vertical data for this analysis to effect a connection between the two sampling methods. The statistical results and the fitted coefficients are shown in Table 3. From these equations a depth relative concentration profile can be calculated by assuming that P values are equivalent relative to depth (examination of several profiles supported the assumption).

The vertical profile results (equation 4, Table 3) can be combined with the trajectory time–dilution equations (equation 2, Table 2) to calculate time–depth distribution of relative concentration (Fig. 6), though it should be noted that the time-axis follows lines of isoconcentration rather than extending vertically because of the assumed time-concentration symmetry. The bottom boundary shown in Fig. 6 is derived from a regression between bottom depth and time along the centerline trajectories. PON and DOC show a greater depth penetration with time than Na while POC behaves similarly to Na.

The results of areal development analysis (Fig. 4) can now be mapped onto the vertical profile model (equation 4, Table 3) to allow calculation

TABLE 3. Fitted coefficients and statistical results of regressions using equation (4) for vertical profile data.

Variable	Coefficients a	b_1	b_2	b_3	b_4	Regression F-value	df	r
Na	−4.768	−0.466	1.040	0.932	−0.196	578.97	4,147	0.970
DOC	−3.999	−0.168	0.642	0.493	—	548.82	3,190	0.947
POC	−4.633	−0.149	0.807	—	−0.087	477.03	3,156	0.950
PON	−3.064	−0.177	0.619	—	−0.030	3459.26	3,273	0.987

[a] Only coefficients entering a stepwise multiple regression significantly at $P = 0.005$ are included to form the fitted equation.

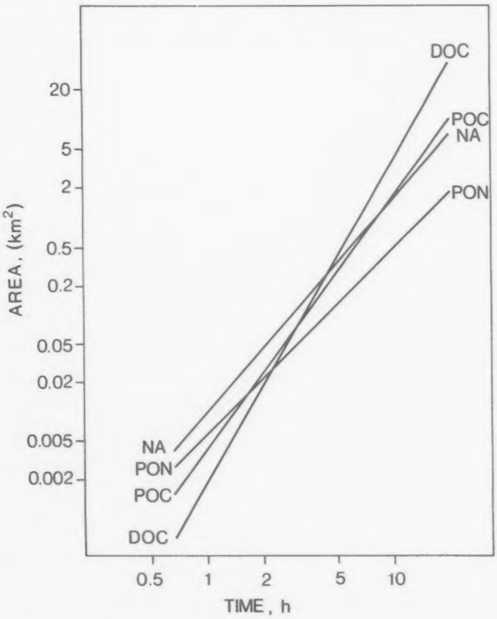

FIG. 5. Predicted area of plume as a function of time–dilution from the effluent source.

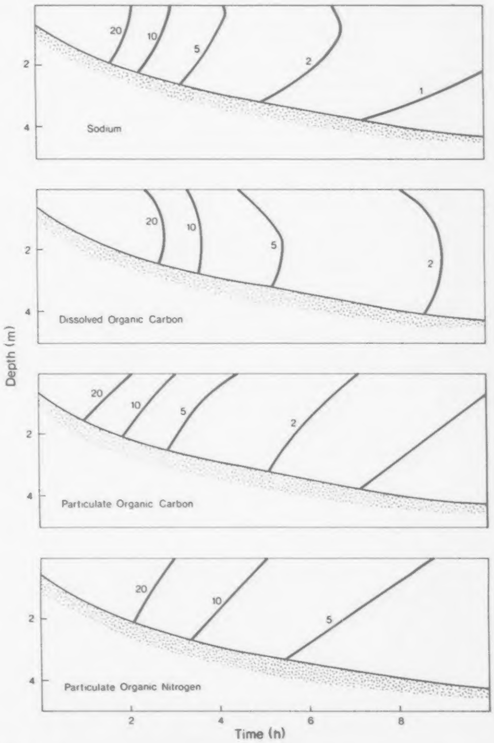

FIG. 6. Predicted dilution isolines along the centerline trajectory relative to depth and time.

of the volume development of the plume, making allowance for the bottom boundary limitation on vertical development close to the outfall (Fig. 7). Volume development is defined as the growth in volume bounded by a surface of fixed relative concentration as the relative concentration declines towards the edge of the plume. The volumes bounded by similar relative concentrations are much greater for PON and DOC than for Na, though the DOC volume is initially less than that for Na. The POC volume is less than that for Na until the relative concentration is approximately 1% which represents the outer limit of visually recognizable plume. Obviously, since the relative concentrations of all four variables in the effluent are 100%, POC, PON, and DOC are undergoing changes other than by dilution in the plume, as represented by the conservative ion sodium (Na).

For each of the chemical variables, bounded volumes were calculated for a representative set of relative concentrations. Dilution time (T) for each variable × concentration pair were calculated under the time–concentration symmetry assumption (equation 2, Table 2). Then an expected mean relative concentration can be calculated with each bound volume by assuming simple dilution of effluent released into the plume in time (T) with background water:

TABLE 4. Computed expected mean relative concentrations and times for a representative set of isoconcentration boundaries.

Synoptic variable		Boundary isoconcentration % 20	15	10	5	2	1
Sodium	$C_{\text{exp-r}}\%$	24.0	18.6	12.3	6.3	2.4	1.1
	T(h)	2.4	2.8	3.4	4.9	7.7	10.9
Dissolved organic carbon	$C_{\text{exp-r}}\%$	31.2	17.9	8.1	2.2	0.4	0.1
	T(h)	2.3	2.7	3.3	4.9	8.1	11.8
Particulate organic carbon	$C_{\text{exp-r}}\%$	59.3	41.1	24.9	10.3	3.3	1.3
	T(h)	2.1	2.4	3.0	4.4	7.2	10.5
Particulate organic nitrogen	$C_{\text{exp-r}}\%$	13.5	8.3	4.0	1.2	0.3	0.1
	T(h)	3.0	3.7	5.1	8.8	17.9	30.7

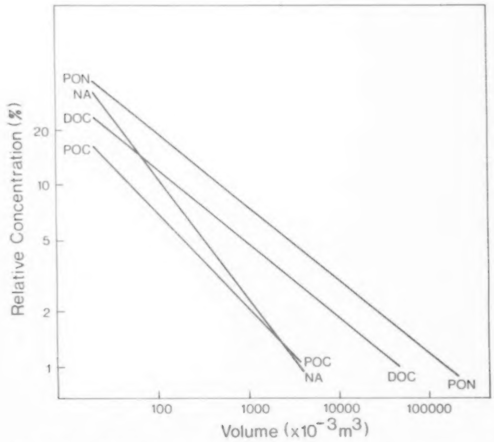

FIG. 7. Predicted volume development versus relative concentration of the effluent plume.

$$(5)\quad C_{\text{exp}} = (V_T \cdot C_e + (V_B - V_T) \cdot C_b)/V_B$$

where C_{exp} = expected mean concentration
V_B = Isoconcentration bound volume
V_T = Inflow of effluent during dilution time (T)
C_e and C_b as in equation (1)

Then the expected mean relative concentration $C_{\text{exp}-r}$ is calculated using equation (1). This value $C_{\text{exp}-r}$ could be compared to a mean relative concentration calculable from the analysis given thus far. However, given the rapid logarithmic decay of concentration observed in the plume, the calculable or analytical mean relative concentration will generally be close to the bounding concentration. In this case, the ratio of $C_{\text{exp}-r}$ to bounding concentration for a conservative substance should be slightly greater than 1. The calculated values for the representative boundary concentrations for the four chemical variables are presented in Table 4, along with the calculated dilution times (T). The ratios are plotted in Fig. 8 using a time X-axis and with all ratios forced to have the expected value of 1 at time zero, i.e. the effluent at discharge time.

Sodium, as expected, appears to be conservative with ratio values of 1.1–1.2 for boundary concentrations between 20 and 1% (Fig. 8). The ratios for the other three variables indicate considerable divergence from conservatism. Ratios greater than those of sodium indicate a loss other than by dilution, while ratios less than those of

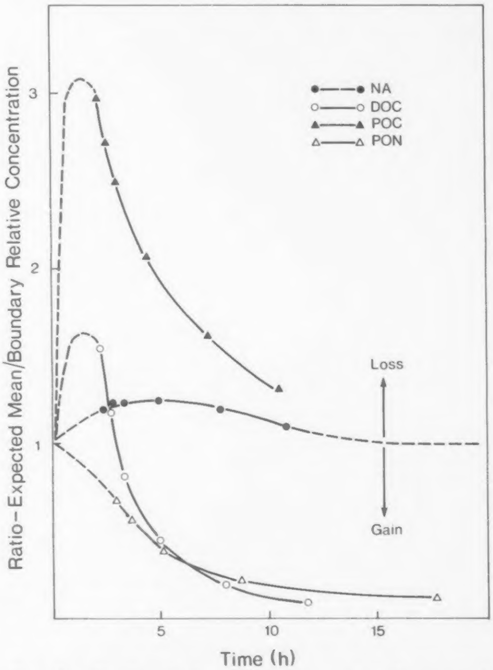

FIG. 8. Predicted changes in the ratio of expected mean concentration to boundary concentration versus time in the effluent plume.

sodium indicate a gain. The curve for POC indicates a loss from the plume within the first 2 h but later tends towards a balancing with sodium. DOC also exhibits a loss in the first 2 h which is redressed by a gain latterly while PON shows a gain in the first 5–8 h. After about 10 h, all the ratios change very slowly indicating a maintained equilibrium.

Discussion

Particulate organic carbon (POC) and nitrogen (PON) are generally treated as being coupled in limnological studies. In natural systems, they can be expected to increase as a result of autotrophic and heterotrophic production and to decrease as a result of degradation and sedimentation. However, in the pulp and paper mill effluent plume, POC exhibits a loss followed by a recovery while PON is gained in the plume with the rate of gain declining latterly. Thus POC and PON are not homogeneously associated in the particulate pool in the effluent plume. There can be no doubt that sedimentation loss of a particulate fraction (mostly fibrous material not removed by the clarifier) occurs in the immediate vicinity of the outfall and that that fraction has a lower than average PON:POC ratio. The increase in total PON indicates particulate production at concentrations of effluent which must be the result of heterotrophic rather than the autotrophic activity since Moore and Love (1977) observed a marked reduction in primary production in relative concentrations of effluent greater than 1%. The initial loss of DOC is due to both chemical and biological degradation which accounts for the marked reduction in oxygen content observed beyond the outfall by Johnson (1977). Johnson also showed that aerobic biological degradation has a minimal contribution to caloric changes occurring along the centerline trajectories, so that any significant biological degradation must be anaerobic. Subsequently DOC exhibits a significant recovery and increase which, coupled with the recovery of POC, could be attributed to primary production although still reduced from natural levels.

The rates of production, degradation and sedimentation examined by Johnson (1977) in the surface centerline trajectory are insufficient to explain estimated mass-balance changes occurring in the total plume. However, there are aspects of the outfall area which can qualitatively correct any imbalances. In the vicinity of the outfall the bottom consists of old fiberbeds which accumulated over many years prior to the introduction of clarifier and discontinuing of waterboom entry of logs into the mill. These beds are subject to degradation which could result in the release of DOC into the plume which predominately traverses shallow areas. Further turbulent mixing in these shallow areas could result in continual resuspension of particulate matter. Thus, this analysis of plume, while providing some knowledge of changes other than by dilution, is probably confounded by the local physiochemical environment into which the effluent is released.

Conclusions

1) On average, the plume occupies a surface area of about 1.5 km^2 at the 1% relative concentration level (derived from the equation for sodium in Fig. 4). This area is equivalent to the plume area that might be generated if the discharge were the cooling water of a small power plant (Elliott and Harkness 1972). However, the potential biological impact is far greater for pulp and paper mill effluent as evidenced by the biological studies in this volume.

2) The analysis indicates a significant interaction between the bottom substrate in the vicinity of the outfall and the plume which necessarily confounds any interpretation of processes other than dilution occurring in the plume. Thus any attempt via materials–balance methods to evaluate the impact of a pulp and paper mill effluent must allow for carryover effects of prior operating conditions.

Acknowledgments

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ASHBURY, J. G., AND A. A. FRIGO. 1971. A phenomenological relationship for predicting the surface areas of thermal plumes in lakes. Argonne Nat. Lab. Rep. No. ANL/ES-5.

ELLIOTT, R. V., AND D. G. HARKNESS. 1972. A phenomenological model for the prediction of thermal plumes in large lakes. Proc. Conf. Great Lakes Res. 15: 544–564.

FOX, M. E. 1977. Persistence of dissolved organic compounds in kraft pulp and paper mill effluent plumes. J. Fish. Res. Board Can. 34. (This issue)

INLAND WATERS DIRECTORATE, DEP. OF ENVIRONMENT. 1972. Analytical Methods Manual.

JOHNSON, M. G. 1977. Caloric changes along pulp and paper mill effluents plumes. J. Fish. Res. Board Can. 34. (This issue)

MOORE, J. E., AND R. J. LOVE. 1977. Effect of a pulp and paper mill effluent on the productivity of periphyton and phytoplankton. J. Fish. Res. Board Can. 34. (This issue)

POLICASTRO, A. J. 1972. State-of-the-art of analytical modelling of heated effluent dispersion in large lakes. Proc. Conf. Great Lakes Res. 15: 642–654.

Caloric Changes Along Pulp and Paper Mill Effluent Plumes[1]

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JOHNSON, M. G. 1977. Caloric changes along pulp and paper mill effluent plumes. J. Fish. Res. Board Can. 34: 784–790.

Eight pulp and paper effluent plumes in Nipigon Bay were tracked with Rhodamine dye to determine dilution and nondilution losses of calories with distance and time. Dilution, as determined by Na^+ decrease, accounted for 98.5% of the decrease in caloric concentration along centerline trajectories of plumes over 2000 m in 7.5 h; mean caloric concentration decreased from 1583 cal·ℓ^{-1} in effluent to 50 cal·ℓ^{-1} at background stations. Nondilution caloric changes were estimated by two methods, first by examination of the main processes (respiration, settling of particles, and primary production) and, secondly, by interpretation of time series of direct measurements of caloric concentrations. By the first method, measurement of respiration indicated loss of 2.1 cal·ℓ^{-1}, while particle loss from plumes was 25.5 cal·ℓ^{-1} and accrual of calories by primary production was 0.5 cal·ℓ^{-1}. Integration of these results yielded an estimate of 27.1 cal·ℓ^{-1} net nondilution loss in caloric concentration along centerline trajectories over the average distance of 2000 m. By the second method, direct measurement of decrease in caloric concentration gave an estimate of nondilution loss of 45 cal·ℓ^{-1} over 2000 m. Approximately 17% of effluent calories were used in biodegradation and lost in sedimentation from the plume within 2000 m of the source. Environmental degradation, in terms of dissolved oxygen conditions and deposition of particles, apparently was only locally significant.

JOHNSON, M. G. 1977. Caloric changes along pulp and paper mill effluent plumes. J. Fish. Res. Board Can. 34: 784–790.

La couche superficielle d'effluents de huit moulins de pâte et de papier dans la baie Nipigon a été suivie à l'aide du colorant rhodamine dans le but de déterminer les pertes de calories par dilution et non-dilution en fonction de la distance et du temps. La dilution, déterminée par le diminution de Na^+, est responsable de 98.5% de la diminution de concentration calorique le long de la trajectoire de la ligne centrale des couches superficielles sur une distance de 2 000 m en 7.5 h; la concentration calorique moyenne diminue de 1 583 cal·ℓ^{-1} dans l'effluent à 50 cal·ℓ^{-1} aux stations d'arrière-plan. Deux méthodes ont servi à estimer les changements caloriques non dus à la dilution : la première, un examen des processus principaux (respiration, sédimentation des particules et production primaire) et la seconde, l'interprétation de séries chronologiques de mesures directes des concentrations caloriques. Dans la première méthode, les mesures de respiration indiquent une perte de 2.1 cal·ℓ^{-1}, alors que la perte par sédimentation est de 25.5 cal·ℓ^{-1} et que les calories dérivées de la production primaire sont de 0.5 cal·ℓ^{-1}. En intégrant ces résultats, on arrive à un estimé de 27.1 cal·ℓ^{-1} de perte nette par non dilution de concentration calorique le long des trajectoires de la ligne centrale sur une distance moyenne de 2 000 m. Dans la seconde méthode, les mesures directes de diminution de concentration calorique donnent un estimé de perte par non-dilution de 45 cal·ℓ^{-1} sur une distance de 2 000 m. Environ 17% des calories de l'effluent sont utilisées dans la biodégradation et perdue par sédimentation de la couche superficielle en dedans de 2 000 m de la source. Il semble que la dégradation de l'environnement, en termes d'oxygène dissous et de déposition des particules, a une signification locale seulement.

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PULP and paper mill effluents have been of concern in water pollution abatement programs primarily because of high potential input of suspended solids and oxygen-consuming materials to natural systems. Consequently, earliest abatement technology was aimed at control of solids and BOD. However, provided that implementation of such

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

controls is adequate for protection of receiving waters in specific cases, other effluent components are of concern, specifically those which are toxic to aquatic life or impart undesirable flavors to fish. The purpose of this paper is to examine the fate of solids and BOD inputs by measuring both in calories and determining losses in transit in plumes.

Suspended solids and BOD inputs are considered, in simplest conceptual terms, as inputs of allochthonous energy to be dispersed, utilized through heterotrophic processes in the water, and deposited, in part, on bottom sediments where an additional fraction of the energy may be used. This study deals with the input of organic matter, its dilution in plumes in time and space toward background concentrations, and specifically with losses in heterotrophic processes in plumes and settling of particles from plumes. Primary production must be considered in this concept as an energy-fixing process within the plume. Each of these three processes may be measured, but it is also possible to determine the collective change due to these processes by direct measurement of decrease in caloric content of plume waters, providing that the decrease in calories due solely to dilution can be determined. In this study sodium ion was used to determine dilution, made possible because of the high concentration (over 100 $\mathrm{mg \cdot \ell^{-1}}$) in effluent and low concentration (about 1 $\mathrm{mg \cdot \ell^{-1}}$) in receiving water. Results obtained by the two methods are presented here, obtained first by measurement of respiration and particle loss with a correction for accrual of energy fixed in primary production and, secondly, by examination of nondilution decrease in caloric concentration. The work was carried out in July 1974, together with other studies (Fox 1977, Minns 1977), along the centerline trajectory of eight plumes in Nipigon Bay of Lake Superior (Fig. 1). The bay receives effluent (about 73 $\mathrm{m^3\ min^{-1}}$) from a mixed-groundwood, kraft-pulping plant at Red Rock, Ont., which employs a clarifier for suspended solids removal.

Materials and Methods

Approximately 1.0 ℓ of dye solution (Rhodamine WT dissolved in acetic acid and mixed with methanol to produce a specific gravity of 1) was added to the effluent channel at a point immediately before its discharge. Subsequently the center of the spreading "dye-blob" was located by making two or more transects to find the point of maximum concentration of Rhodamine WT using a continuous flow fluorometer. Water samples were taken and the dye concentration was reinforced with a further addition. Position of the station was obtained on radar by the vessel *Porte Dauphine*. In this manner, the effluent plume was "tagged" and sampled four to six times over a period of several hours. Concentration of dye solution of several μg/ℓ was too low to interfere with the processes under study. The effluent plume and the dye-blob were usually concentrated within the top 1 m of the water column. Water samples and dye measurements were taken at 0.5 m or, when the plume was deeper, by an integrated pumped sample taken through the plume depth. Water samples were taken at eight stations remote from the plume to estimate background concentrations of materials of interest in water masses likely to be entrained by the plume.

Sodium was determined by an automated flame photometric method (Technicon Corporation 1974).

Caloric concentrations were determined on separated particulate and dissolved fractions. Particulate material was separated by settling and centrifugation and frozen in the field laboratory. Subsequently, each fraction was evaporated at room temperature, dried overnight at 60 C, desiccated in tared aluminum pans and weighed on a Cahn Electrobalance to obtain dry weight. Two pellets of each sample (one only when particulate mass was small) were burned in a Phillipson micro-bomb calorimeter (Phillipson 1964) with a small quantity of refined fuel oil of known caloric content.

Particle concentrations and size distribution were determined with a Coulter Counter Model B and Millipore Particle Measurement Computer System. (For a full description of the technique, see Leslie 1977.) To maintain independence between the two methods, caloric content of particles determined by one method was not used in the second; instead the caloric content of particulate matter, obtained by Leslie's method, was assumed to be 5.0 $\mathrm{cal \cdot mg^{-1}}$. Results were not available for Plume J18 but estimates were made from data on particulate organic carbon based on Leslie's regression (Leslie 1977, Table 2).

Respiration rates in plume samples and oxycaloric equivalents were determined as follows: Duplicate 250-ml gas bottles of water were incubated in darkness at 20 C; dissolved oxygen concentration was measured (with YSI Model 54 oxygen meter) at the time of temperature equilibration and again after approximately 24 h. Depletion rates were converted to calories using the factor 3.4 cal/mg dissolved oxygen (Slobodkin 1962). Plume water temperatures ranged from 16 to 22 C and, in view of this relatively narrow range, no temperature adjustment was applied to depletion rates determined at 20 C. Some samples were treated with formalin to measure COD (Chemical Oxygen Demand). Only full-strength effluent had a substantial COD relative to total oxygen demand and the biological component of oxygen demand was taken as 0.75 of the total in effluent samples.

Experimental data on primary production (Moore and Love 1977) were used as estimates of energy fixation in the plume. Results from incubations at optimum light and effluent dilution of 10^{-2} were considered to be applicable to plumes over 6–9 h.

Rates measured in mg $C \cdot \ell^{-1} \cdot h^{-1}$ were converted to calories on the assumption that dry weight was 40% carbon and 5.0 cal/gm dry weight.

This analysis, applied to data on calories and particles, consisted of the following steps: concentrations of calories and particles together with sodium were each scaled to values of 0–1.0 using the equation

$$C' = (C - C_b)/(C_e - C_b)$$

where C' is the scaled value of caloric or particle or sodium concentration, C is the concentration in a specific plume sample, and C_e and C_b are effluent and mean background concentrations, respectively.

Each plume series for each of calories and particles was examined stepwise to calculate C' "expected" through dilution alone as determined by change in sodium C' from each station to the next in the series. Differences between observed and "expected" scaled concentrations of calories and particles, that is, the change due to nonconservative processes, were converted to real concentrations in the equation

$$\Delta C = \Delta C' \ (C_e - C_b)$$

In Method One the net loss of calories was estimated as the sum of particle loss (nondilution decrease in particle weight through sedimentation and decomposition losses, converted to calories) plus the caloric equivalent of measured oxygen consumption rates minus energy fixation in primary production processes.

In Method Two net loss of calories was measured directly as the nondilution change in concentration of total calories. The only common feature of the two methods is that nondilution change in particles (obtained by Leslie's technique) in Method One and nondilution change in calories (obtained by calorimetry) in Method Two were determined by comparison with Na^+ decrease, as described previously.

Results

CALORIES, PARTICLES, AND Na^+

Effluent samples, taken at the point of discharge to Nipigon Bay, had average caloric concentrations of 1583 $cal \cdot \ell^{-1}$ (1295 dissolved, 288 particulate), 75.87 $mg \cdot \ell^{-1}$ particles and 130 $mg \cdot \ell^{-1}$ Na^+. Background concentrations averaged 26.5 $cal \cdot \ell^{-1}$ (24.6 dissolved and 1.9 particulate), 1.91 $mg \cdot \ell^{-1}$ particles and 1.55 $mg \cdot \ell^{-1}$ Na^+ (Table 1).

Of the eight plumes studied, four travelled upshore further into the bay in a northwesterly direction, two alongshore southeasterly to Five Mile Point and two offshore in an easterly direction (Fig. 1). The distance travelled by dye-blobs in plumes was 1100–2590 m (average of 2000 m) over 6.0–8.8 h (average of 7.5 h). The average dye-blob velocity was 7 $cm \cdot s^{-1}$.

Dilution, as determined by Na^+ decrease, accounted for 98.5% of the decrease in caloric concentration along plume centerline trajectories; mean caloric concentration decreased from 1583 to 50 $cal \cdot \ell^{-1}$, which was only 23.5 $cal \cdot \ell^{-1}$ above background. Time-weighted mean concentrations were 265 $cal \cdot \ell^{-1}$ and 14.76 $mg \cdot \ell^{-1}$ of particles equivalent to 73.8 $cal \cdot \ell^{-1}$.

DISSOLVED OXYGEN

Effluent samples contained 2.1–6.9 $mg \cdot \ell^{-1}$ dissolved oxygen, but lower concentrations, less than 1.0 $mg \cdot \ell^{-1}$, were observed in the bay within 100 m of the outfall. Recovery in oxygen content was rapid and all samples beyond approximately 200 m contained at least 8.0 $mg \cdot \ell^{-1}$ Average dissolved oxygen concentrations at the eight "end-of-plume" stations and eight "background" stations were 9.3 and 9.8 $mg \cdot \ell^{-1}$, respectively. Oxygen concentration in effluent and along plume paths, when plotted (Fig. 2) against total caloric concentration, shows the oxygen sag and subsequent recovery in relation to oxygen available, substrate concentration (calories) and effluent dilution (Na^+).

DILUTION OF EFFLUENT

The dilution of Na^+ was as great as to within 0.1 $mg \cdot \ell^{-1}$ of background Na^+ concentration (the limit of detection of a difference from back-

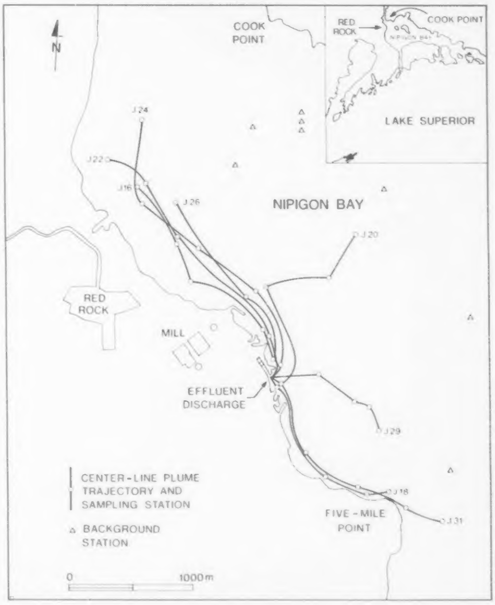

FIG. 1. Paths of eight plumes and sampling stations, Nipigon Bay, July 1974.

TABLE 1. Observed concentrations and scaled concentrations (C') of sodium, total calories and particles at each station along centerline trajectories in the eight plumes examined, together with time and distance of travel.

Plume		Sodium		Total calories		Particles	
Distance (*m*)	Time (*h*)	mg·ℓ^{-1}	C'	cal·ℓ^{-1}	C'	mg·ℓ^{-1}	C'
Background stations		1.6		26.5		1.91	
			Plume J16				
70[a]	1.0	48	1.0	557	1.0	43.68	1.0
420	3.0	12.6	0.237	107	0.152	n.d.	—
1150	4.3	3.6	0.043	46	0.037	3.54	0.039
1480	6.5	3.4	0.039	43	0.031	4.45	0.061
2050	8.1	3.3	0.034	45	0.035	4.85	0.070
			Plume J18				
100[a]	1.0	76	1.0	798	1.0	70.0	1.0
930	3.3	13.3	0.157	44	0.023	10.56	0.127
1280	5.4	8.2	0.089	69	0.055	5.84	0.058
1420	7.6	14.3	0.171	114	0.113	8.28	0.094
			Plume J20				
0	0	140	1.0	1840	1.0	102.23	1.0
100	1.9	5.5	0.028	57	0.017	2.88	0.010
780	4.1	3.5	0.014	48	0.012	2.28	0.004
1310	5.9	2.5	0.007	42	0.008	1.94	0.001
1340	7.4	1.7	0.001	32	0.003	2.53	0.006
			Plume J22				
0	0	160	1.0	1844	1.0	66.53	1.0
360	1.1	35	0.211	397	0.204	6.97	0.078
1440	3.3	3.6	0.013	33	0.004	3.94	0.031
1950	4.8	3.4	0.012	41	0.008	2.67	0.012
2320	7.0	3.3	0.011	61	0.019	4.22	0.036
			Plume J24				
0	0	100	1.0	1429	1.0	71.40	1.0
130	1.2	53	0.522	265[b]	0.170	12.37	0.151
750	2.8	8.8	0.073	68	0.030	3.35	0.021
1320	5.5	3.4	0.018	48	0.015	2.18	0.004
1910	7.0	2.7	0.011	41	0.010	2.26	0.005
2590	8.8	2.4	0.008	38	0.008	2.21	0.004
			Plume J26				
0	0	113	1.0	1258	1.0	86.17	1.0
190	2.0	17.7	0.145	175	0.121	8.31	0.076
740	4.8	3.4	0.016	38	0.009	5.05	0.037
1680	6.0	2.8	0.011	38	0.009	3.02	0.013
			Plume J29				
0	0	104	1.0	1310	1.0	62.03	1.0
410	1.6	6.1	0.044	49	0.018	4.63	0.045
780	3.9	2.8	0.012	41	0.011	3.18	0.021
900	6.0	2.5	0.009	32	0.004	2.16	0.004
1100	7.7	2.2	0.006	34	0.006	2.44	0.009
			Plume J31				
0	0	163	1.0	1819	1.0	66.89	1.0
680	1.6	6.1	0.028	52	0.014	3.76	0.028
1130	3.5	8.8	0.045	66	0.022	4.25	0.036
1500	5.8	8.1	0.040	70	0.024	3.39	0.023
1810	7.5	4.5	0.018	39	0.007	2.94	0.016

[a] No effluent samples for these two plumes.

[b] Spurious value indicated by calorie–organic C relationship (unpublished data), therefore omitted in stepwise calculation of nondilution loss of calories.

TABLE 2. Comparison of results obtained by direct measurement of processes and by measurement of nondilution change in concentration of calories (all values in cal$\cdot\ell^{-1}$).

	Direct measurement of net loss				Loss calculated from nondilution change in caloric concentration
Plume	Respiration	Sedimentation	Primary production	Net loss	
J16	3.1	−8.2	−0.5	−5.6	40
J18	2.9	20.0	−0.5	22.4	65
J20	1.8	7.1	−0.4	8.5	7
J22	1.6	32.0	−0.4	33.2	0
J24	1.8	128.2	−0.5	129.5	135
J26	2.5	21.9	−0.4	24.0	31
J29	1.5	−1.2	−0.5	−0.2	26
J31	1.7	3.9	−0.5	5.1	27
All plumes	2.1	25.5	−0.5	27.1	45

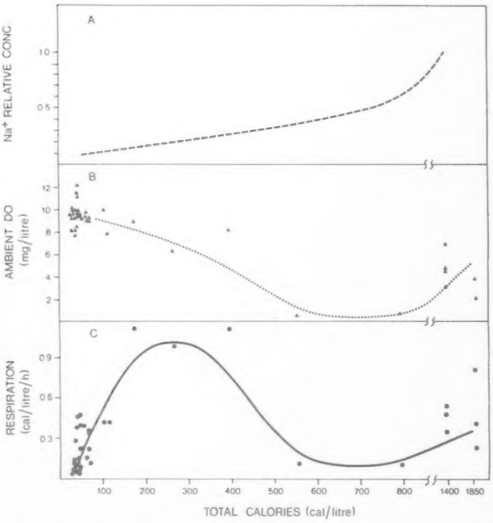

FIG. 2. Relationship among respiration rate in plume samples, dilution of effluent, ambient dissolved oxygen concentration and caloric concentration. (A) Relative sodium concentration averaged for all plumes to indicate dilution of effluent, (B) Ambient dissolved oxygen concentration in relation to caloric concentration, (C) Respiration rate in relation to caloric concentration. Data on effluent samples are those values to right of break in abscissa. The curves are not mathematically fitted to these data.

ground) in 7.4 h in the offshore plume J20 and as low as nine times background in 7.6 h in plume J18 (Table 1). In the other six plumes concentrations of Na^+ of 2.2–4.5 mg$\cdot\ell^{-1}$, averaging twice the background concentration of 1.6 mg$\cdot\ell^{-1}$, were observed in the mean time of 7.5 h and mean distance of 1925 m from source.

LOSS OF CALORIES — METHOD ONE

Three components are assessed in the first method, nondilution decrease in particle concentration, respiration, and accrual of calories through primary production.

Particle losses, assumed to be mainly through sedimentation from the plumes, varied between −8.2 cal$\cdot\ell^{-1}$ (a gain in particles occurred in Plume J16 which traversed the inshore zone to Five Mile Point, as shown in Fig. 1) and 128.2 cal$\cdot\ell^{-1}$. Losses averaged 25.5 cal$\cdot\ell^{-1}$ in the eight plumes (Table 2), corresponding to a mean loss of mass of particles of 5.1 mg$\cdot\ell^{-1}$.

The three primary factors governing respiration rate are temperature, oxygen supply and substrate supply. Temperature was relatively constant at 16–22 C. Respiration rate was related to both ambient dissolved oxygen concentration and total caloric concentration representing potentially available substrate (Fig. 2). Respiration rates were intermediate in level in undiluted effluent averaging 0.48 cal$\cdot\ell^{-1}\cdot h^{-1}$ at high substrate concentrations and intermediate levels of dissolved oxygen. Respiration rates were lowest, approximately 0.10 cal$\cdot\ell^{-1}\cdot h^{-1}$, when ambient dissolved oxygen was less than 1 mg$\cdot\ell^{-1}$. Respiration rates were greatest averaging 1.09 cal$\cdot\ell^{-1}\cdot h^{-1}$ at relatively high concentrations of oxygen and caloric concentrations of 200–400 cal$\cdot\ell^{-1}$. Rates declined to 0.17 cal$\cdot\ell^{-1}\cdot h^{-1}$ at the eight "end-of-plume" stations which had mean substrate concentration of 50 cal$\cdot\ell^{-1}$ (Fig. 2). Time-integrated respiration averaged 2.1 cal$\cdot\ell^{-1}$ over 7.5 h, representing the nondilution decrease in calories due to energy use in biodegradation processes along plume centerline trajectories.

Estimated increase in caloric concentration due to primary production was 0.4–0.5 cal·ℓ^{-1} through the same time period.

Through synthesis of these estimates, net nondilution loss of calories from centerline plume samples averaged 27.1 cal·ℓ^{-1}, but varied between −5.6 cal·ℓ^{-1} (in Plume J16 with apparent accrual of particles) and 129.5 cal·ℓ^{-1} (Table 2).

LOSS OF CALORIES — METHOD TWO

Direct calculation of nondilution loss of calories yielded results generally greater than estimates by the first method. Caloric losses averaged 45 cal·ℓ^{-1}, compared with a mean of 27.1 cal·ℓ^{-1} obtained by Method One (Table 2). In six of eight plumes estimates by Method Two were greater. Plume J24 had the greatest calculated loss, in which case, results from the two methods were in close agreement (Table 2).

Discussion

Caloric content of pulp mill wastewater effluent was substantial, averaging nearly 1600 cal·ℓ^{-1}. In theory, nearly 500 mg of oxygen per litre of wastewater would be consumed in its degradation through aerobic metabolism. The relatively refractive nature of the organics was indicated by average respiration rates of only approximately 0.2 cal·ℓ^{-1}·h^{-1} and utilization of only 1.5–3 cal·ℓ^{-1} over 6.0–8.8 h, that is, only 0.55–1.1% of the time-weighted mean concentration of 265 cal·ℓ^{-1} in plumes.

Respiration was controlled by oxygen supply, substrate availability, as implied by concentration of calories, and apparently inhibitory concentrations of wastewater components in the undiluted effluent. At concentrations of effluent below approximately 20% (indicated by the scaled concentration of Na^+ in Fig. 2), respiration was proportional to caloric concentration up to approximately 300–400 cal·ℓ^{-1} and dissolved oxygen concentration exceeded 6.0 mg·ℓ^{-1}. This relationship applied to most of the plume volume, but respiration was inhibited close to the effluent canal because, although caloric concentration was about 500–800 cal·ℓ^{-1}, ambient dissolved oxygen was extremely low and probably the limiting factor. In diluted effluent, with 1300–1800 cal·ℓ^{-1}, respiration was relatively low, apparently not because oxygen was depleted, but more likely because of inhibition by components of the effluent at their greatest concentrations.

Loss of calories in particles, presumably mainly through sedimentation, was at least ten times as great as use of calories in biodegradation processes (Table 2). Generally sedimentation loss was a function of particle concentration, but this relationship did not prevail when plumes traversed shallow, inshore areas, as for example in the case of Plume J16. Inshore plumes may receive as well as deposit particulate matter and entrain dissolved organics at the water–sediment interface. Also, varying conditions of current and turbulence within the plume could affect sedimentation. Particulate and dissolved fractions could interact, with solution of organics from particles and adsorption and precipitation of dissolved compounds (as pH declined from alkaline to slightly acidic) being possible processes. These were not investigted, nor was the problem examined in assuming that rates of diffusion and advection which affect Na^+ movement are similar to those which affect particle transport.

Comparison of the centerline loss of calories, 45 cal·ℓ^{-1} calculated by Method Two, with the time-weighted mean concentration of 265 cal·ℓ^{-1} in plumes indicates that approximately 17% of effluent calories were used or lost through sedimentation over 7.5 h within approximately 2000 m of the outfall. Further losses would be expected to occur beyond 2000 m but the methods used in this study are not sufficiently precise to deal effectively with samples only marginally greater in caloric concentration than background. Furthermore, the ecological impact would be minor at greater distances. Caloric concentration had decreased to 50 cal·ℓ^{-1} at 2000 m, and dilution accounted for 98.5% of the observed decline.

The average particle loss of 25.5 cal·ℓ^{-1} (5.1 mg·ℓ^{-1}), compared with the time-weighted mean concentration of particles of 73.8 cal·ℓ^{-1} (14.76 mg·ℓ^{-1}), indicated a loss of 35% of particles within 2000 m of the outfall. This loss represents 26.25 mg·ℓ^{-1} of the original 75.87 mg·ℓ^{-1} in effluent samples. Assuming that most of the loss was sedimentation, the deposition rate would approach 1800 mg·m^{-2}·day^{-1} using Minns' area of plume development of 1.5 km^2 at 2000 m (Minns 1977). The total area within 2000 m of the outfall is 6.3 km^2 (semicircle of radius 2000 m); therefore, the long-term deposition rate would approach 430 mg·m^{-2}·day^{-1} over 6.3 km^2, that is about 2100 cal·m^{-2}·day^{-1}. This is not particularly high in comparison with the few published results, for example, approximately 800–6900 cal·m^{-2}·day^{-1} in Prince Edward Bay and the Bay of Quinte, Lake Ontario (Johnson and Brinkhurst 1971). However, the qualitative effect of continuous fiber input to sediments, especially at greater rates in the inshore area closest to the outfall, would be expected to affect the benthic community locally.

These data suggest that energy use and uptake of oxygen in aerobic degradation of organics and sedimentation of particulate matter and its deposition apparently were not proceeding at rates deleterious to receiving waters in Nipigon Bay except very locally. Furthermore, relative to findings (for example, Fox 1977), it would appear desirable, in both research and abatement technology, to emphasize work on the persistence, effects on the biota, and possible remedial measures of so-called trace organics which may be toxic or which may taint fish potentially available for commercial and recreational fishing.

Acknowledgments

Assistance of Wayne Hyatt in field studies and Christel Charlton in analysis of caloric concentrations, both of Great Lakes Biolimnology Laboratory, is appreciated. Cooperation of many units at C.C.I.W. was vital to the successful completion of the Red Rock studies. C. K. Minns of G.L.B.L. offered several suggestions for analysis of data for this report.

Fox, M. E. 1977. Persistence of dissolved organic compounds in kraft pulp and paper effluent plumes. J. Fish. Res. Board Can. 34: (This issue)

Johnson, M. G., and R. O. Brinkhurst. 1971. Benthic community metabolism in Bay of Quinte and Lake Ontario. J. Fish. Res. Board Can. 28: 1715–1725.

Leslie, J. K. 1977. Characterization of suspended particles in some pulp and paper mill effluent plumes. J. Fish. Res. Board Can. 34. (This issue)

Minns, C. K. 1977. Analysis of a pulp and paper mill effluent plume. J. Fish. Res. Board Can. 34. (This issue)

Moore, J., and R. J. Love. 1977. Effect of a pulp and paper mill effluent on the productivity of periphyton and phytoplankton. J. Fish. Res. Board Can. 34. (This issue)

Phillipson, J. 1964. A miniature bomb calorimeter for small biological samples. Oikos 15: 130–139.

Slobodkin, L. B. 1962. Energy in animal ecology, p. 69–101. *In* J. B. Cragg [ed.] Advances in ecological research. Academic Press, Inc. New York, N.Y.

Technicon Corporation. 1974. Technicon Autoanalyzer Methodology N-20B. Tarrytown, N.Y.

Characterization of Suspended Particles in Some Pulp and Paper Mill Effluent Plumes[1]

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LESLIE, J. K. 1977. Characterization of suspended particles in some pulp and paper mill effluent plumes. J. Fish. Res. Board Can. 34: 791–797.

Some physical characteristics of the suspended particles from seven pulp mill effluent plumes were analyzed electronically. An effluent flow rate of 1.2 $m^3 \cdot s^{-1}$ contained a mean of 75.9×10^9 $\mu m^3 \cdot \ell^{-1}$ particulate volume in a size range of 3.2–84.0 μm "diameter." The visible particle surface area was 334.8 $cm^2 \cdot \ell^{-1}$, and there were 1045×10^3 $particles \cdot ml^{-1}$. A slight increase in size was detected as the particles aged in the plume. The transported particulates were reduced by dispersion and sedimentation to approximately 5% by a transit of less than 1 km, but effluent was still detectable 2 km from the point source.

LESLIE, J. K. 1977. Characterization of suspended particles in some pulp and paper mill effluent plumes. J. Fish. Res. Board Can. 34: 791–797.

Nous avons analysé électroniquement certaines caractéristiques physiques des particules en suspension provenant de la couche superficielle de l'effluent de sept usines de pâte. Un taux d'écoulement d'effluent de 1.2 $m^3 \cdot s^{-1}$ contient un volume moyen de particules de 75.9×10^9 $\mu m^3 \cdot \ell^{-1}$ de tailles comprises entre 3.2 et 84.0 μm de « diamètre ». La superficie des particules visible est de 334.8 $cm^2 \cdot \ell^{-1}$, et il y a $1\,045 \times 10^3$ $particules \cdot ml^{-1}$. Nous détectons une légère augmentation de taille à mesure que les particules vieillissent dans la couche superficielle. La matière particulaire transportée est réduite d'environ 5% par dispersion et sédimentation sur un trajet de moins de 1 km, mais l'effluent est encore détectable à 2 km de la source.

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MUCH of the suspended particulate matter from pulp mill effluents consists of small wood fibers which are potentially harmful, if not destructive, to most organisms of natural aquatic ecosystems. High concentrations of these particulates tend to increase the albedo and alter the heat content of surface waters, scatter solar radiation, and decrease the sunlight available for photosynthetic organisms. The consequences for organisms throughout the food web are often detrimental (Waldichuk 1970; Marier 1973; Schiebe et al. 1975). However, the physical effects of excessive particle concentrations on biota in general are mostly speculative but are ultimately related to primary production.

A knowledge of the physical characteristics of particulates enhances the understanding of their life span in the water column. Information concerning the physical characteristics of particles and their entrainment in discharged pulp mill wastewater is useful in evaluating the extent and impact of the contaminants on aquatic species and communities. The quantification of surface area, volume, and number of particulates entrained in seven pulp mill discharge plumes from a Nipigon Bay point source are described in this paper.

Materials and Methods

Quantitative samples were taken at a single depth along single line tracks; neither horizontal nor vertical dispersion about or beyond these points was considered in this study. Serial sampling was terminated approximately 2 km from the source, though the plume was usually visible beyond.

Estimates were made of mean particle volume, visible area, and number at the discharge and succeeding points along the plume. Particulate organic carbon and nitrogen were also measured and related to particle physical characteristics.

Forty samples from seven different plumes (Fig. 1)

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

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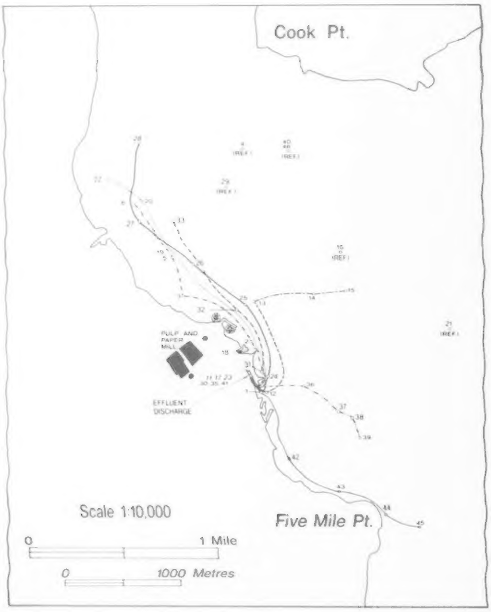

FIG. 1. Plume tracks and sampling sites in Nipigon Bay.

that emanated from a mixed groundwood efflux of of 1.2 $m^3 \cdot s^{-1}$ were taken in conjunction with plume centerline trajectory tracking (dye blob studies). Each sample was preserved with 1 ml Lugol's iodine for quantitative particle analyses. Water samples for chemical analyses were taken simultaneously. The organic carbon and nitrogen content of particulate samples collected on precombusted Whatman GF/C filters were determined with a CHN Analyzer (Hewlett-Packard 185).

Electronic counters (Leslie et al. 1973) were used to measure the visible surface area and the equivalent volume. Estimates of particle number and visible area of suspended particulates were obtained with a Millipore Particle Measurement Computer System. This unit utilizes a vidicon camera for optical sensing of 10 levels of subject greyness. A Wild M40 inverted microscope presents the image of settled particulates to the vidicon, and the resulting video signals are analyzed in the computer modules. Areal image analysis involves the detection of particles as they have randomly settled on a plane surface, and measurements are therefore referred to as "visible surface area." This variable relates to the square of the radius of a sphere, rather than the cube of its diameter. Maximum horizontal chord, the greatest horizontal internal chord of a particle, was measured in the range of 3.2–84.0 μm for size distributions in 14 size intervals. Depending on effluent concentration, 1 or 10 ml of subsample was added to a 50 ml settling column containing filtered (0.45 μm) distilled water, and allowed to settle overnight. For the determination of total number of particles and total particulate area, 40 vidicon fields were counted and averaged in each size interval. The instrument calibration was checked with a stage micrometer and National Bureau of Standards slide. Calibration was kept below 0.5% deviation.

A Coulter Counter Model B was used to estimate size distribution, volume, and number of particles in 14 size intervals in the 3.2–84.0 μm "equivalent" diameter range. For practical purposes, this diameter was assumed equivalent to a sphere of the same volume as the measured particle. Spherical particles were rare in the kraft mill effluent, however, hence the term "equivalent" diameter. A tube with a 100 μm aperture was used for particles up to 6.4 μm diameter; for all other sizes, a 200 μm aperture was used. Spherical pollen of 19.5 μm diameter was used for calibration of both apertures.

Samples from the discharge site only were washed through a 100 μm mesh to prevent aperture clogging. They were then diluted 100-fold and all others 10-fold using filtered (0.45 μm) 0.8% saline solution. Blank counts were subtracted from all sample counts.

Results

Measurements of volume, surface area, organic carbon, and number, of particles in all samples near (100–410 m) the point source indicated that the effluent suspended load (seston), decreased by at least 80% along the plumes' centerline trajectory. An additional 15% reduction occurred from plume transits of less than 1 km (Table 1, Fig. 1 and 2). Plume samples 13, 25, 32, 37 and 38, and 42, which were 680–900 m from the discharge, contained particulates whose physical characteristics were generally within a few percent of corresponding reference samples 16, 29, 33 (terminal sample), 40, and 46, respectively (Fig. 3). In most cases, heavy loading was evident only in the vicinity of the discharge (Fig. 2).

The mean value of discharged particulate volume was 75.9×10^9 $\mu m^3 \cdot \ell^{-1}$ (Table 1). Based on the assumption that the specific gravity of all discharge particles was 1.5, the estimate of the mean particulate mass at the discharge was 114 $g \cdot m^{-3}$. Terminal samples apparently retained 4.1% (3.1×10^9 $\mu m^3 \cdot \ell^{-1}$) of the effluent, and comparative reference samples showed a mean of 2.1×10^9 $\mu m^3 \cdot \ell^{-1}$. Thus, the discharge load was 25 times that at terminal sites and 36 times greater than the reference particulates. Discharge values exclude sample 1, which was taken 70 m from the source and was thus not a true "discharge" sample.

The mean values of total particulate visible surface area in discharge, terminal, and reference samples were 334.8 $cm^2 \cdot \ell^{-1}$, 12.1 $cm^2 \cdot \ell^{-1}$, and 10.6 $cm^2 \cdot \ell^{-1}$, respectively (Table 1). The total

TABLE 1. Physical and chemical analyses of pulp mill effluent, Nipigon Bay.

Sample	Seston volume ($10^9\ \mu m^3 \cdot \ell^{-1}$)	Total visible area ($cm^2 \cdot \ell^{-1}$)	Ratio A:V	Particulate organic carbon (mg/ℓ)	Particulate organic nitrogen (mg/ℓ)	Particle number × 10^3 per ml (Coulter)	Particle number × 10^3 per ml (Millipore)	Distance from discharge (m)
1	43.7	190.9	4.4	14.7	0.42	589	412	70
3	3.5	15.3	4.4	1.3	0.07	43	41	1150
*4R	1.5	7.6	5.1	0.6	0.04	24	21	2060
5	4.5	20.4	4.5	1.1	0.06	51	46	1480
6T	4.8	25.3	5.3	1.0	0.06	43	63	2050
11D	102.2	452.2	4.4	17.1	0.39	1422	988	0
12	2.9	15.3	5.3	1.0	0.06	36	42	100
13	2.3	13.3	5.8	0.6	0.04	33	33	780
14	1.9	10.4	5.5	0.3	0.05	29	34	1310
15T	3.9	11.0	2.8	0.6	0.05	48	34	1580
16R	2.5	12.1	4.8	0.4	0.04	26	34	1340
17D	66.5	233.9	3.5	19.4	0.48	838	633	0
18	7.0	35.5	5.1	5.1	0.18	155	95	360
19	3.9	9.7	2.5	0.5	0.05	55	29	1440
20	2.7	11.9	4.4	0.6	0.06	40	42	1950
21R	2.9	16.3	5.6	0.3	0.03	40	49	1720
22T	4.2	13.2	3.1	0.7	0.07	55	44	2320
23D	71.4	512.2	7.2	39.0	0.54	1109	1894	0
24	12.4	87.7	7.1	3.3	0.14	210	200	130
25	3.3	14.4	4.4	2.3	0.12	45	33	750
26	2.2	8.1	3.7	0.5	0.05	24	25	1320
27	2.3	13.3	5.8	0.5	0.04	28	35	1910
28T	2.2	11.1	5.0	0.5	0.05	30	32	2590
29R	2.4	13.0	5.4	0.7	0.11	22	17	1780
30D	86.2	354.9	4.1	20.3	0.27	1119	752	0
31	8.3	27.0	3.3	2.2	0.09	128	70	190
32	5.1	14.1	2.8	0.6	0.07	42	42	740
33T	3.0	10.0	3.3	0.6	0.06	34	29	1680
35D	62.0	232.5	3.8	19.7	0.49	988	600	0
36	4.6	17.8	3.9	1.1	0.06	64	47	410
37	3.2	15.8	4.9	0.6	0.05	38	40	780
38	2.2	10.4	4.7	0.5	0.04	26	33	900
39T	2.4	13.2	5.5	0.4	0.03	33	30	1100
40R	1.5	7.8	5.2	0.2	0.02	20	19	2030
41D	66.9	223.0	3.3	20.6	0.47	796	521	0
42	3.8	12.6	3.3	0.8	0.06	44	44	680
43	4.2	18.2	4.3	1.0	0.06	58	56	1130
44	3.4	18.2	5.4	1.8	0.11	49	54	1500
45T	2.9	14.1	4.9	1.1	0.07	39	40	1810
46R	1.2	3.7	3.1	0.4	0.04	11	12	2030
Mean (exclusive of samples 1–6)								
*D = discharge	75.9	334.8	4.4	22.7	0.44	1045	898	
T = terminal	3.1	12.1	4.1	0.7	0.06	40	35	
R = reference	2.1	10.6	4.8	0.4	0.05	24	26	

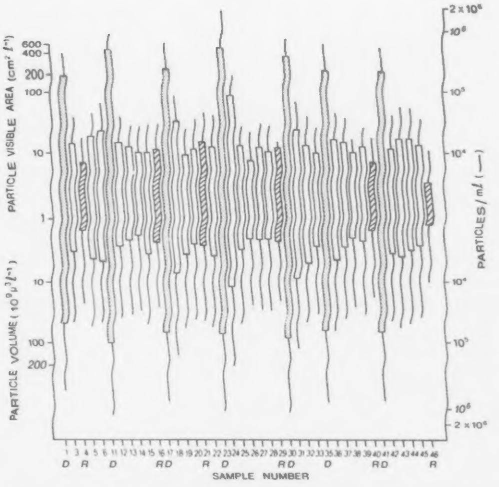

FIG. 2. Particle volume, visible area, and number of particles in Nipigon Bay samples. Symbols: D, discharge; T, terminal; R, reference.

visible area of discharge particulates averaged 28 times that of terminal particles and 32 times the area of reference particles.

In terms of particle number determinations, terminal samples apparently contained approximately 4% of the original effluent suspended matter, in which there was a mean Coulter count of 1045 × 10^3 particles·ml^{-1} and a Millipore count of 898 × 10^3 particles·ml^{-1}.

There were five instances in which there were gains in the entrained particulate load (Fig. 2). A greater abundance of particles in reference sample 21 than in some of the related plume samples was apparent. Reference samples 16, 21, and 29 contained particles whose volume and area exceeded those of some plume samples.

The biochemical variables of particulates, organic carbon (POC), and nitrogen (PON), followed the same trend as seston particle volume and area, i.e. exhibiting high values near the discharge, then declining to reference sample levels as the plume coursed into the bay (Table 1, Fig. 2). The parallel decline of values of physical

TABLE 2. Log–log regression of particulate area and volume (3.2–84.0 μm diameter) on POC and PON (all sizes of particles).

Y	X	Intercept	r
$\log_{10}$ area $(\text{cm}^2 \cdot \ell^{-1})$ =	0.8472 $\log_{10}$ POC (mg/ℓ)	+ 1.2680	0.950
$\log_{10}$ volume $(10^9\ \mu\text{m}^3 \cdot \ell^{-1})$ =	0.8453 $\log_{10}$ POC (mg/ℓ)	+ 0.6264	0.951
$\log_{10}$ area $(\text{cm}^2 \cdot \ell^{-1})$ =	1.2766 $\log_{10}$ PON (mg/ℓ)	+ 2.7730	0.903
$\log_{10}$ volume $(10^9\ \mu\text{m}^3 \cdot \ell^{-1})$ =	1.3507 $\log_{10}$ PON (mg/ℓ)	+ 2.2046	0.926

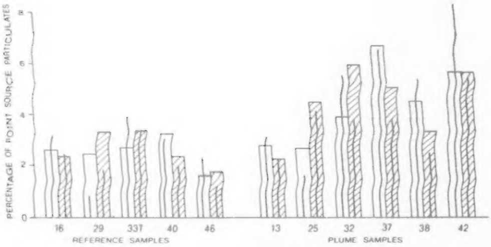

FIG. 3. Total of particles (vertical lines), area, and volume (hatched), at reference sites and at plume sites less than 1 km from the point source, expressed as percentage of discharge particulates.

variables and POC along the centerline of the plume was between 93 and 99%, occasioned by a maximum transit of 900 m. Limits that were set for the size range of particles (3.2–84.0 μm) measured electronically were not imposed for POC determinations. Nevertheless, Table 2 shows the close correlation ($r = 0.95$) of particulate area and volume with POC.

The mean value of POC from point source samples was 22.7 mg/ℓ while that of PON was 0.44 mg/ℓ (Table 1). These values are comparable to those found by Beak (1974) in which nonsettleable solids contained 17–25% organic carbon and 0.8–1.8% organic nitrogen. Terminal sample POC and PON levels were respectively, 3.1 and 13.6% of discharge levels. For all seven plumes examined, approximately 30% of the seston volume and 7% of its visible surface area was POC. Reference sample PON values did not relate well with volume and area determinations (Fig. 4), but PON and the physical variables as a whole appeared to define the plumes' sestonic content reasonably well, and were highly correlated (Table 2).

In all typical discharge samples (Fig. 5A) there was an apparent linear decrease in the number of particles with increasing particle diameter, plotted in log-normal form. The maximum number of particles always occurred in the smallest size range and no particles larger than 51 μm diameter were counted with the Coulter Counter.

The lower optical Millipore counts in the first range were probably the result of instrument insensitivity at the lowest threshold, but the graph (Fig. 5B) does disclose the difference in quantification of the same objects by two different types of sensors. The two graphs of Fig. 5 do not differ radically, yet optical counts suggest greater heterogeneity of particulates in the discharge effluent than resistive counts reveal. The optically-counted 3.2 to 6.3 μm size fraction formed 64% of all discharge seston and 70% each of terminal and reference counts. Particles with a horizontal chord greater than 10.1 μm were slightly more abundant in discharge samples (12%) than in terminal (7%) or reference (9%) samples. In view of the narrow particle size spectrum detected, the density of most particles was therefore similar.

Figure 6 is a plot of particulate volume with a closed size distribution of particle diameters 3.2–84.0 μm for two typical discharge, terminal, and reference samples. The distribution of particulate volume in discharge samples 11 and 23 decreased regularly throughout the size range to about 16 μm diameter, whereas related terminal samples 15 and 28 contained a greater proportion of total volume in a wider spectrum of particle sizes. The graph of samples 16 and 29 illustrates the more diverse particle community of reference waters. Mean particle area:volume ratios (Table 1), were slightly lower (4.1) in distant plume samples than in point source (4.4) and reference samples

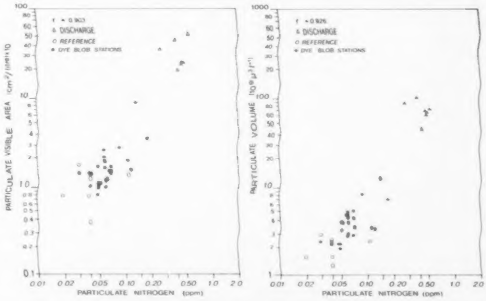

FIG. 4. Relationship between visible surface area, volume, and PON of particles in plume and reference samples.

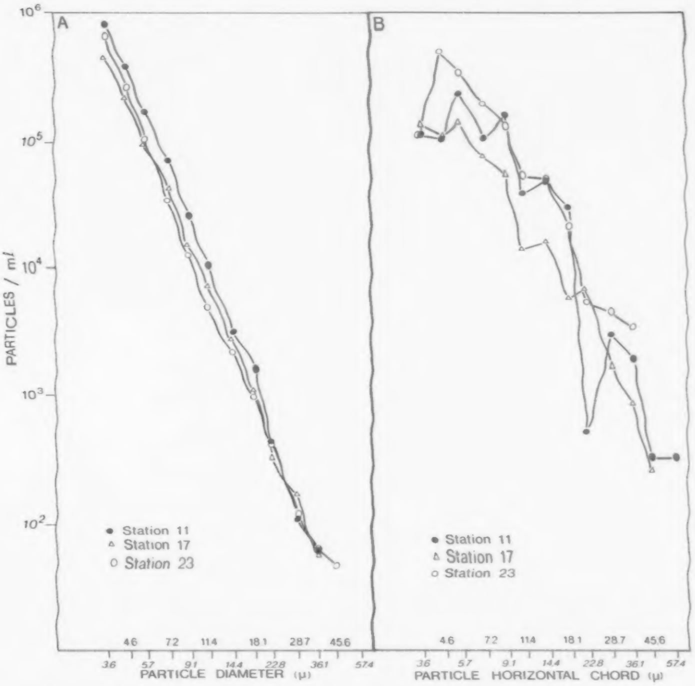

FIG. 5. Coulter (A) and Millipore (B) counts and sizes of particles in typical discharge samples.

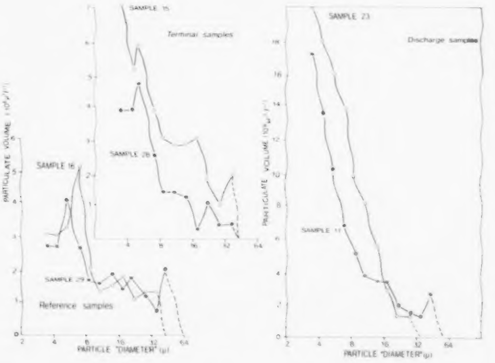

FIG. 6. Relationship between volume and diameter of related discharge, terminal and reference particulates.

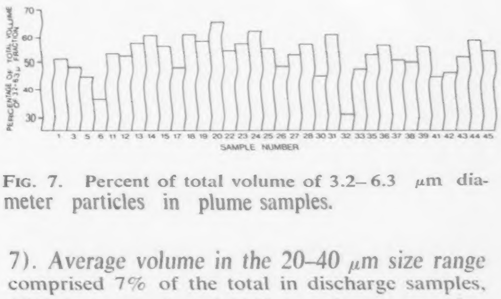

FIG. 7. Percent of total volume of 3.2–6.3 μm diameter particles in plume samples.

(4.8). Particle size distribution became more variable as the effluent dispersed; on average, 52% of sestonic volume in all samples was contained in the 3.2 to 6.3 μm fraction. There was little evidence of systematic change in the relative volume of this fraction along the trajectories (Fig. 7). Average volume in the 20–40 μm size range comprised 7% of the total in discharge samples, 12% in terminal, and 11% in reference samples. Particles changed during transit in the plume as the average particle volume in dilute effluent was 34% greater than discharge particles, which were 5.0 μm average diameter. Reference waters contained particles whose diameter averaged 5.6 μm.

Discussion

The mill effluent was a shallow layer 1–2 m deep, seldom traversing depths greater than 10 m; it generally moved parallel to the shore, as expected from Csanady's (1970) model.

There was no clear distinction between the particles' physical and biochemical characteristics in some of the distant plume samples and those of reference sites. Suspended particulates at reference stations were occasionally more abundant than at terminal sites, and also exceeded levels at some other plume sites.

The influence on seston quantity and character by autochthonous particles or from sediment induced into the plume by physical processes in the bay was not generally known but plume overrun of the nearshore shallows doubtless accounted for gains through resuspension of sediment in serial samples 3 and 5; 5 and 6; and 20 and 22. In addition, negative settling (Burns and Pashley 1974) could have contributed to an increase in seston, especially in deep water, and to the development of PON in the plume. The choice of reference sites had been somewhat arbitrary, but evidently they should have been more widely removed from the contaminated area.

Bewers and Pearson (1972), using a high-speed centrifuge, determined a suspended load of 227 $\mathrm{mg} \cdot \ell^{-1}$ at the outfall of a Nova Scotia kraft mill. Fifty-one percent of the particulates was contained in the 0.10–5 μm fraction. A mean concentration of 66.6 $\mathrm{mg} \cdot \ell^{-1}$ of suspended solids from the clarifier effluent of a bleached kraft mill was reported by Beak (1974). High-speed centrifugation and image analysis techniques assessed the mean diameter of "nonsettleable" particles at 7.1 μm. From these and our own data it appears that most of the suspended particulates from kraft mill effluent are probably less than 10 μm.

Particles larger than 51 μm in diameter, although not apparent in the plume samples, were not necessarily absent. The frequency of occurrence of large particles usually will be very low relative to the small particles but similar amounts of seston exist in logarithmetically equal size-classes (Sheldon et al. 1972).

Particle area, volume, and number are significant in particle transport and sedimentation because they are related to frictional resistance within the water. Particles with a large surface: volume ratio offer more resistance to sedimentation and would therefore tend to remain in the water column longer. This would favor the dispersion of fine particles. Changes in all particle characteristics are brought about by simultaneous processes, such as decay and synthesis; colonization of internal and external surfaces by bacteria and protozoans (Rodina 1966); adsorption and mineralization (Werner 1965); selection by detritivores (Gliwicz 1969), and in turbulent conditions, constant compression and expansion of contained gas bubbles.

The ratio of particulate area:volume provides an indication of particle physical form and history. For example, elongate, "young" discharged particles would eventually become "mature" (Rodina 1966) in the bay as they were colonized and decomposed by bacteria, thus effecting an increase in shape factor and a decrease in the area:volume ratio. The electronic devices used in the present study signified that most samples contained particulates of high area:volume ratio, and that the ratio decreased perceptibly as the plume moved to terminal sites, indicating an ageing of elongate wood fiber, or similar matter.

Samples with low effluent retention possibly contained a large fraction of particles of minerogenic origin from the Nipigon River. Relative to wood fiber, mineral particles usually have a shape factor of lower value, a smaller ratio of area to volume, and higher specific gravity. Conversions from Coulter particle volume to mass would underestimate the seston in these samples.

The scale of surface variation is a significant factor in total surface image measurement (Dahl 1973); therefore, since surface image definition was lacking, the visible surface index (ratio of actual surface to that of a plane with similar boundaries) was unity in this study. The electronic sensors were well suited to the tracing and quantification of a discharge of generally homogeneous, elongate objects such as wood fiber. Particle number and volume best estimate quantity, while area also describes qualitative or historical change. However, the track of single particles cannot be predicted (Weidmann and Sendner 1972), especially in the highly variable water mass of Nipigon Bay.

Particle survey and characterization can define the sphere of influence of the suspended load but biological surveys provide the only real evidence of effects. Recent studies (German 1966; Cooley 1977; Kelso 1977; Vander Wal 1977) concerning the influence of the Nipigon Bay wastewater discharge have shown that certain tolerant species of zooplankton, bottom fauna, larval and adult fish were in notable abundance near the outfall. Particulate analysis showed that discharged wood fiber rapidly dispersed and settled once the plume freed itself from the immediate confines of the discharge area, but was still occasionally evident at points approximately 2 km distant.

BEAK, T. W. 1974. The nature, fate and impact of settleable and nonsettleable solids. 1. Characterization of primary solids. CPAR proj. 241. Consult. Rep. 24 p.

BEWERS, J. M., AND G. J. PEARSON. 1972. The behaviour of particulate material in the treatment lagoons of a bleached kraft pulp mill. Water Air Soil Pollut. 1: 347–358.

BURNS, N. M., AND A. E. PASHLEY. 1974. In situ measurement of the settling velocity profile of particulate organic carbon in Lake Ontario. J. Fish. Res. Board Can. 31: 291–297.

COOLEY, J. M. 1977. Filtering rate performance of *Daphnia retrocurva* in pulp mill effluent. J. Fish. Res. Board Can. 34. (This issue)

CSANADY, G. T. 1970. Dispersal of effluents in the Great Lakes. Water Res. 4: 79–114.

DAHL, A. L. 1973. Surface area in ecological analysis: quantification of benthic coral-reef algae. Mar. Biol. 23: 239–249.

GERMAN, M. J. 1966. Preliminary report of the biological survey of Nipigon Bay 1966. Ont. Water Resour. Comm. Rep. 19 p.

GLIWICZ, Z. M. 1969. The food sources of lake zooplankton. Ekol. Pol. Ser. B 15: 205–223 (Transl. from Polish by Fish. Res. Board Can. Transl. Ser. No. 2716.

KELSO, J. R. M. 1977. Density, distribution, and movement of Nipigon Bay fishes in relation to a pulp and paper mill effluent. J. Fish Res. Board Can. 34. (This issue)

LESLIE, J. K., ET AL. 1973. A comparison of electronic particle counters and inverted microscope methods for counting phytoplankton. Fish. Res. Board Can. Tech. Rep. 394: 31 p.

MARIER, J. R. 1973. The effects of pulp and paper waste with particular attention to fish bioassay procedures for assessment of harmful effects. NRC (Natl. Res. Coun. Can.) Publ. No. BY 73-3 (ES): 33 p.

RODINA, A. G. 1966. Variety and destruction of lake detritus. Verh. Int. Ver. Limnol. 16: 1513–1517.

SCHIEBE, F. R., J. C. RITCHIE, AND J. R. MCHENRY. 1975. Influence of suspended sediment on the temperatures of surface waters of reservoirs. Verh. Int. Ver. Limnol. 19: 133–136.

SHELDON, R. W., A. PRAKASH, AND W. H. SUTCLIFFE JR. 1972. The size and distribution of particles in the ocean. Limnol. Oceanogr. 17: 327–340.

VANDER WAL, J. 1977. Relation between Nipigon Bay benthic macro-invertebrates and selected aspects of their habitat. J. Fish. Res. Board Can. 34. (This issue)

WALDICHUK, M. 1970. Industrial pollution I. Effects of non-metallic contaminants. Fish. Res. Board Can. MS Rep. 115: 110 p.

WEIDMANN, H., AND H. SENDNER. 1972. Dilution and dispersion of pollutants by physical processes. *In* Marine pollution and sea life. Fishing News (Books) Ltd., London.

WERNER, A. E. 1965. Suspended solids from mill effluents. Can. Pulp Pap. Ind. April: 109–114.

Persistence of Dissolved Organic Compounds in Kraft Pulp and Paper Mill Effluent Plumes[1]

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FOX, M. E. 1977. Persistence of dissolved organic compounds in kraft pulp and paper mill effluent plumes. J. Fish. Res. Board Can. 34: 798–804.

The persistence of dissolved organic compounds in the effluent plumes of a pulp and paper mill on the north shore of Lake Superior was studied in 1974. Approximately 90 organic compounds were observed of which 36 (including all the major ones) were identified.

The dispersion of five of these compounds was examined quantitatively. Dehydroabietic acid was the only major organic compound observed to exhibit measurable persistence >2000 m from the effluent discharge. At 2000 m from the discharge, levels of ~ 30 $\mu g/\ell$ dehydroabietic acid were detected within the plume and ~ 15 $\mu g/\ell$ outside the effluent plume. The disappearance of dehydroabietic acid parallels that of the conservative ion Na$^+$, indicating dilution by the receiving water as the only significant short-term removal mechanism.

FOX, M. E. 1977. Persistence of dissolved organic compounds in kraft pulp and paper mill effluent plumes. J. Fish. Res. Board Can. 34: 798–804.

On a étudié en 1974 la persistance des composés organiques dissous dans les couches superficielles de l'effluent d'un moulin de pâte et de papier sur la rive nord du lac Supérieur. Environ 90 composés organiques ont été trouvés, dont 36 (incluant tous les composés majeurs) ont été identifiés.

Nous avons étudié quantitativement la dispersion de cinq de ces composés. L'acide déshydroabiétique est le seul composé organique majeur montrant une persistance mesurable à plus de 2 000 m de l'émissaire de l'effluent. A 2 000 m de l'émissaire, on détecte des niveaux de ~ 30 $\mu g/\ell$ d'acide déshydroabiétique dans la couche superficielle et ~ 15 $\mu g/\ell$ en dehors de la couche superficielle de l'effluent. La disparition de l'acide déshydroabiétique évolue parallèlement à celle de l'ion conservateur Na$^+$, ce qui indique que la dilution par l'eau réceptrice est le seul mécanisme important d'enlèvement à court terme.

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PULP and paper mill effluents comprise one of the major polluting discharges into Lake Superior and have been implicated in oxygen depletion, toxicity, and production of taste and odor in the receiving water and its aquatic communities. Dissolved organic compounds are known to cause much of the acute toxicity to fish of pulp and paper mill effluents (Leach and Thakore 1973; Rogers et al. 1975) and may contribute a significant proportion of taste and odor problems in fish (Thomas 1973; Shumway and Palensky 1973).

This study sought to determine the fate and effective zone of persistence of dissolved organic compounds in pulp and paper mill effluent plumes. A preliminary study of a pulp mill effluent plume at Marathon, 1973, determined the feasibility of unproven laboratory and field techniques and led to significant changes in plume tracking and sample processing. Subsequently, the more protected Red Rock mill site was selected to examine the behavior of persistent organic compounds in pulp mill plumes.

Field Studies — Red Rock 1974

The Red Rock site, where a bleached kraft and ground wood paper mill discharges 96,500 m^3/day of clarified effluent into Nipigon Bay, has a low nearshore wave energy due to the protection afforded by offshore islands and high bluffs to the west. Because of these geographical features, the zone of interaction between the effluent plume and the receiving water was usually much more extensive than that at the Marathon preliminary study site.

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

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Rhodamine WT dye dissolved in acetic acid was mixed with sufficient methanol to give a specific gravity of 1. Approximately 1 ℓ of the dye solution was added to the effluent channel prior to its discharge into Nipigon Bay. Subsequently the center of the dye marker patch was located using a small boat to make two or more transects of the dye patch. A continuous flow fluorometer permitted the detection of the point of maximum concentration of Rhodamine WT and the position was fixed by an anchored radar equipped vessel. Water samples were taken and a further addition of dye was made to form the basis of the next sampling location further along the effluent plume. In this manner, the effluent plume was "tagged" and sampled four to six times over a period of 8–10 h.

Since the effluent is approximately 15 C warmer than the receiving water it has a lower specific gravity. Thus, at most times during the study period, the effluent plume and dye marker patch were concentrated largely within the top m of the water column. Therefore, all water samples and dye concentration measurements were taken at 0.5 meters or by an integrated sample over the plume depth.

Effluent plume tracking and sampling, as described above, was carried out on eight different occasions at 2-day intervals in July 1974. Water samples collected for extraction of dissolved organic compounds ranged in volume from 0.5 ℓ at the effluent discharge point and 3 ℓ in the plume at >1000 m to 4.5 ℓ in "clean" water reference samples and river water samples. All samples were collected in clean amber glass bottles with teflon lined caps and taken immediately to the shipboard laboratory where they were acidified to pH 2.0 with concentrated HCl.

On three of the plume tracking days, reference water samples were taken at 0.5 m in an area of the bay outside the visible plume. One water sample, taken near Vert Island at a distance of 20 km from the mill, was considered to represent a background profile for dissolved organic compounds in Nipigon Bay.

Samples of the Nipigon River, the principal input of dissolved organics other than the Red Rock Mill, were collected from the river mouth and approximately 20 km upstream from the river mouth.

Experimental

EXTRACTION OF DISSOLVED ORGANIC COMPOUNDS FROM WATER

The procedure used to recover dissolved organic compounds from water samples was similar to that of Junk et al. (1974) using XAD-2 macroreticular resin beads, and only differences in procedure will be described.

The XAD-2 resin was purified by washing with distilled water followed by a double Soxhlet extraction with residue free acetone. The purified resin was stored in amber glass battles under "oragnic free" water.

The acidified water samples were passed by gravity flow at approximately 10 ml/min through 10 cm long × 2 cm diameter resin beds in glass tubes.

The loaded columns were eluted with residue free diethyl ether, evaporated down to 1 ml, and stored in glass ampoules after the removal of a 1–5 $\mu\ell$ sample for preliminary gas chromatographic analysis (GC). The samples were refrigerated for more detailed GC and gas chromatography–mass spectrometry (GC–MS) analyses.

EFFICIENCY OF EXTRACTION PROCEDURES

Recovery tests on the XAD-2 columns were performed using pure compounds to represent the classes of organics extracted from the effluent, e.g. monoterpenes, diterpene resin acids, phenols, and fatty acids. These tests indicated good recoveries ranging from 80 to 100%. In some cases, recoveries from the highly concentrated effluent discharge samples were believed to be low. This was thought to be due to precipitation of low solubility free acids upon acidification rather than to poor recoveries. In any event, the recoveries obtained from the effluent plume samples were not affected by this solubility effect since the concentrations of individual compounds were relatively low.

PREPARATION OF EXTRACTS FOR GC AND GC–MS ANALYSIS

The water extracts were each divided into two aliquots. The first aliquot, to be used for direct GC and GC–MS analysis, was made up to a precise volume of 50–200 $\mu\ell$ with acetone after the diethyl ether was evaporated off. The second aliquot was methylated with diazomethane and the final volume adjusted as above. The choice of final volume for each extract solution was based on the preliminary GC run in the field.

GC ANALYSIS OF SAMPLE EXTRACTS

Gas chromatograms of both the methylated and unmethylated sample extracts were run on a Hewlett Packard 5700A Gas Chromatograph equipped with single flame ionization detector and a 1.8 m × 3 mm stainless steel column packed with 3% OV-1 on Chromosorb W-HP 80–100 mesh. Detector temperature was 250 C with hydrogen gas flow rate of 30 ml/min and air flow rate of 240 ml/min. The injection port temperature was 250 C and the nitrogen carrier gas flow rate 25 ml/min. The oven was temperature programmed from 80 to 270 C at 11 C/min after an initial isothermal hold of 4 min.

GC–MS ANALYSIS OF SAMPLE EXTRACTS

A limited, but representative, number of the

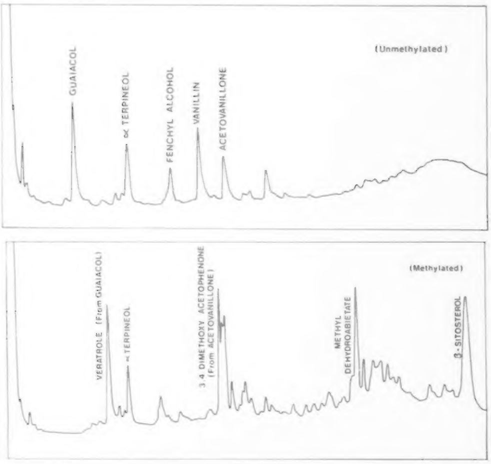

FIG. 1. Chromatogram of extract of effluent at discharge — July 22, 1974.

methylated and unmethylated sample extracts were run on a Finnigan 1015 C GC–MS with computerized data processing. The mass spectra were produced by electron impact at 70 eV. In addition to mass spectra of individual compounds, the computerized data system was used to produce 'Reconstructed Gas Chromatograms' (RGC's) from the total ion current integrated throughout the GC–MS run, and 'Limited Mass Range Chromatograms' (LMRGC's) from the ion current of a single selected mass or set of masses integrated throughout the GC–MS run. The RGC's are essentially similar to a Flame Ionization GC.

Identification of Components

The choice of column and temperature allowed reasonably good separation of the nonacidic components in the unmethylated extracts, but was rather lacking in resolution in the methylated extracts (Fig. 1). In particular, the fatty acid methyl esters and diterpene resin acid methyl esters in the center of the chromatogram were poorly resolved. This compromise in resolution avoided the necessity of the complex separation techniques utilized by other workers in the field (Leach and Thakore 1973; Rogers 1973) with the attendant risk of loss of trace components and could be largely overcome by the use of LMRGC's (Fig. 2). This figure shows the sharp delineation of three significant classes of compounds in the effluent using the computer to plot suitably distinctive LMRGC's. Other mass ranges scanned, such as m/e 149 for phthalic acid esters, are not shown. LMRGC's were used for peak identification only. Quantitation of components was based on the flame ionization chromatograms. Identification of individual mass spectra was achieved mainly through the use of the computerized mass spectral library research system of EPA-Battelle Memorial Institute.[2]

Related Measurements

Subsamples of all plume and effluent samples were shipped to headquarters laboratory and analysed for dissolved organic carbon (DOC) and Na^+. DOC gives an estimate of overall disappearance of dissolved organics while Na^+ represents the disappearance of a conservative species, showing dilution effects only.

Results and Discussion

On the 6 plume tracking days for which data are summarized, the distance travelled by the dye marker in the effluent plume varied from 1450 to 2600 m over periods of 6.5–9 h. The average distance was 2000 m in 8 h or a velocity of 7 cm/s. The predominant plume direction during the study period was to the northwest, parallel to the shore (Fig. 3). Since the plume was largely a surface structure, rarely extending below 1 m, wind was the principal driving force (Polak and Palmer 1976).

From the 29 samples collected from the effluent discharge and effluent plume, some 90 compounds were observed, of which 36 (including all of the major ones) were identified. At distances beyond 2000 m in the plume some 50 compounds were observed at concentrations usually below 10 $\mu g/\ell$ (Table 1). Many of these compounds comprise part of the natural dissolved organics of Nipigon Bay (Table 2). The dissolved organic compounds found in the Nipigon River, which constitutes the major input to Nipigon Bay, are essentially similar, consisting mostly of fatty acids (Table 2).

Early in the study, it was found that the effluent discharge had a characteristic dissolved organic profile, i.e. the same compounds were almost always present and their relative proportions remained quite similar. Because of this observation and the complexity of the spectrum of compounds, only the five organic compounds which were consistently predominant in the mixture were investigated quantitatively.

The five compounds were: guaiacol, a substituted phenol arising from the breakdown of lignin and one of the components known to undergo chlorination in the mill process (Rogers and Keith 1974); αterpineol, a monoterpene alcohol possessing a strong taste and odor, possibly implicated in fish tainting; acetovanillone, also a substituted phenol arising from the breakdown of lignin; dehydroabietic acid, a diterpene resin acid known to be acutely toxic to fish at less than 2 mg/ℓ (Rogers 1973); and β-sitosterol, a phytosterol occurring at high concentration in the effluent and moderately persistent in the plume.

Guaiacol, αterpineol, and acetovanillone

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[2] Now incorporated into the 'Cyphernetics' system.

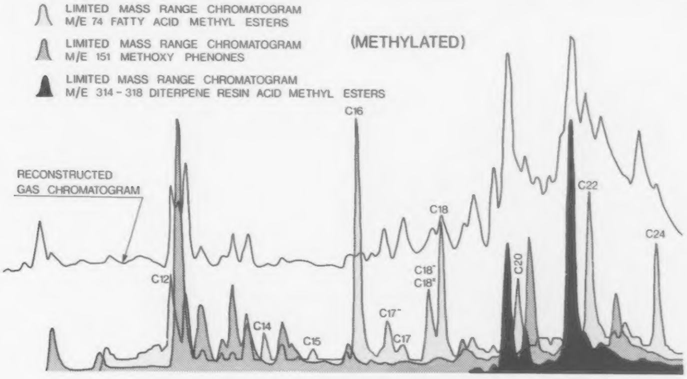

Fig. 2. Limited mass range chromatogram of extract of effluent at discharge — July 16, 1974.

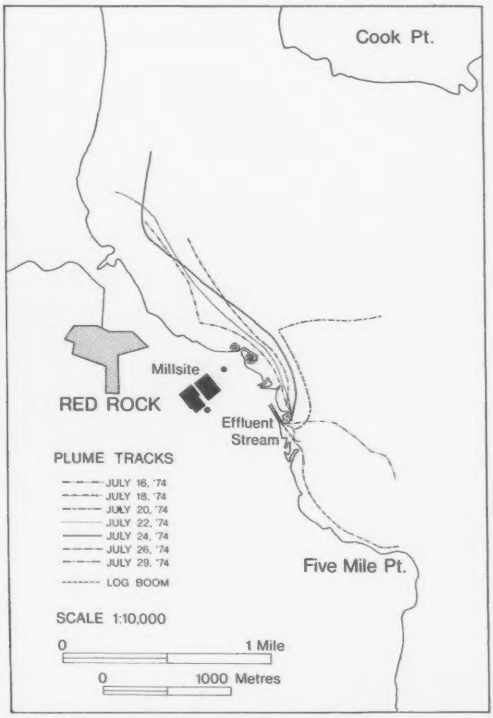

Fig. 3. Effluent plume tracks at Red Rock, Ont.

dropped to almost undetectable concentrations when Na+ was <3 mg/ℓ, i.e. about twice the background level of 1.5 mg/ℓ. These compounds, which were not detected in the reference samples, may be removed from the plume by the processes of bacterial degradation and volatilization. Guaiacol has been implicated in fish tainting at concentrations of >10 μg/ℓ (Shumway and Palensky 1973). αterpineol has an odor threshold (350 μg/ℓ) 100-fold greater than that of guaiacol (3 μg/ℓ) (Buttery et al. 1971), while acetovanillone has no taste or odor. Consequently, the maximum effective zone of impact for fish tainting would be less than 1000 m for guaiacol and much less than that for αterpineol. No fish tainting effects would be expected from acetovanillone. Sublethal effects of these compounds, other than the tainting of fish flesh, have not been considered here due to a lack of published data on the subject.

β-sitosterol is a plant sterol of relatively high molecular weight and low volatility. Its concentration falls off somewhat more slowly than the more volatile compounds considered and it is presumed to undergo bacterial degradation and possibly accretion onto particulate material in addition to dilution with the receiving water. In areas outside the plume, it is generally below the detection limits of this study. β-sitosterol has not previously been implicated in toxicity or tainting studies.

Dehydroabietic acid, of intermediate molecular weight and low volatility, is the single major effluent component observed in measurable quantities in the receiving water at distances in excess of 2000 m from the source (Table 3).

Disappearance due to bacterial degradation appears slow and dilution appers to be the most significant short-term removal mechanism as seen from a comparison with the disappearance of the conservative ion, Na+ (Table 3). At ~2000 m from the effluent discharge, 10–40 μg/ℓ dehydroabietic acid is found within the plume while at comparable distances outside the plume a back-

TABLE 1. Dissolved organic compounds identified in the Red Rock Mill effluent and effluent plume. Major components >100 $\mu g/\ell$, minor components <100 $\mu g/\ell$ in effluent.

Compound	Major component	Minor component	Detected in effluent	Detected in effluent plume
β-pinene		+	+	−
Camphene		+	+	−
Guaiacol	+		+	+
Borneol		+	+	+
Fenchyl alcohol	+		+	+
Safrole[a]		+	+	+
αterpineol	+		+	+
Phenol		+	+	−
2-methoxy-4-propyl phenol		+	+	−
Vanillone		+	+	−
Acetovanillone	+		+	+
Trichloroguaiacol		+	+	−
4-hydroxy-3-methoxy propiophenone[a]	+		+	+
4-hydroxy-3-methoxy phenyl acetic acid		+	+	−
Epijuvabione		+	+	−
Myristic acid		+	+	+
Pentadecanoic acid		+	+	−
Palmitic acid	+		+	+
Heptadecanoic acid		+	+	−
Stearic acid	+		+	+
Arachidic acid	+		+	+
Behenic acid	+		+	+
Lignoceric acid	+		+	+
Palmitoleic acid		+	+	+
Oleic acid	+		+	+
Linoleic acid	+		+	+
Isopimaric acid	+		+	+
Sandaracopimaric acid		+	+	+
Dehydroabietic acid	+		+	+
Abietic acid	+		+	+
6, 8, 11, 13 abietatetraen-18-oic acid		+	+	+
7-oxodehydroabietic acid		+	+	+
Dehydrodiconiferyl alcohol[a]		+	+	−
β-sitosterol	+		+	+
Dimethyl phthalate		+	+	+
Dioctyl phthalate		+	+	+

[a] Tentative identification.

ground concentration of $\sim 15 \mu g/\ell$ dehydroabietic acid is observed. This background level of dehydroabietic acid in the water is not maintained at greater distances from the discharge as seen from the trace level observed near Vert Island, approximately 20 km from the discharge (Table 2).

Dehydroabietic acid was also detected in the Nipigon River (Table 2) at up to 15 $\mu g/\ell$ and averaging 5 $\mu g/\ell$. This river was used for log drives to the mill for many years. Leaching of dehydroabietic acid from sunken logs may account for the levels observed in the river. This is supported by the fact that no dehydroabietic acid was detected in the nearby Jackfish River which was not used for log drives.

Also detected in the plume, although present in minor quantities, was a related compound, 7-oxodehydroabietic acid, identified in environmental samples for the first time by Brownlee and Strachan (1977). 7-oxodehydroabietic acid occurs in the effluent discharge and plume samples at approximately one tenth of the dehydroabietic acid levels and appears to exhibit about the same degree of persistence. The highly toxic

TABLE 2. Dissolved organic compounds found off Vert Island at 1 m (Nipigon Bay background profile for dissolved organic compounds) and Nipigon River water (Principal source of input to Nipigon Bay other than the Red Rock Mill).

Compound	Detected off Vert Island 1 m	Detected in Nipigon River mouth 1 m
Lauric acid	—	+
Myristic acid	+	+
Pentadecanoic acid	+	+
Palmitoleic acid	+	+
Palmitic acid	+	+
Heptadecanoic acid	+	+
Linoleic acid	+	−
Oleic acid	+	+
Stearic acid	+	+
2-methyl octadecanoic acid	+	−
n-Tetracosane	+	−
Arachidic acid	+	+
Lignoceric acid	−	+
Di-butyl phthalate	+	−
Di-octyl phthalate	+	+
Di-hexyl adipate	−	+
Dehydroabietic acid	+	+

TABLE 3. Concentrations of selected organic compounds, dissolved organic carbon, and sodium in the effluent plume on 2 representative days.

Distance from source *(m)*	D.O.C. *(mg/ℓ)*	Na$^+$ *(mg/ℓ)*	Guaiacol *(μg/ℓ)*	αterpineol *(μg/ℓ)*	Aceto-vanillone *(μg/ℓ)*	Dehydro-abietic acid *(μg/ℓ)*	β-sitosterol *(μg/ℓ)*
Dye run #4 July 22, 1974							
0	182.0	160.0	1145	600	1265	1225	1090
300	47.0	35.0	740	350	570	1930	480
1400	9.5	3.6	18	14	5	140	35
1900	8.0	3.4	8	7	1	60	18
2300	7.0	3.3	2	2	ND[a]	35	6
1700[b]	5.5	1.5	ND	ND	ND	18	ND
Dye run #5 July 24, 1974							
0	128.0	100.0	7040	7895	5065	9065	2400
100	65.0	53.0	595	430	510	545	520
750	14.0	8.8	60	50	60	295	85
1300	7.0	3.4	4	1	18	120	30
1900	6.5	2.7	< 1	< 1	1	25	5
2600	6.0	2.4	ND	ND	< 1	40	1
1650[b]	5.5	2.0	ND	ND	ND	35	ND

[a] Not detected.

[b] Reference sample — outside plume area.

mono and dichloro dehydroabietic acids recently reported by Leach and Thakore (1975) were not observed in this study.

Although a wide range of fatty acids were detected in the effluent and effluent plume (Table 2), some of which are known to be toxic to fish at the low milligrams per litre level, they have not been considered since, at the extreme dilutions encountered in the plume, the levels observed are not readily distinguishable from background levels. The natural production of these acids in both lakes and rivers, is felt to be such that the greatly diluted effluent does not exert a significant effect beyond a few hundred meters.

Among other compounds noted in the effluent plume, receiving waters and tributary rivers

(Tables 1 and 2) were phthalic acid esters (PAE's). No satisfactory interpretation for the presence of these ubiquitous materials is offered. PAE's find widespread industrial application as plasticizers, pesticide carriers and additives to industrial oils. Although no use of PAE's at the Red Rock Mill is recorded, dioctyl phthalate was observed, on one occasion, as a major component in the mill effluent. The presence of dioctyl phthalate in the Nipigon River and the sample off Vert Island could be accounted for by uptake from the atmosphere as has been suggested by other researchers (Morita et al. 1974), or by laboratory contamination of the samples. The latter explanation is not considered likely in view of the precautions taken and the production of blanks free from this component.

Several highly toxic chlorinated organic compounds arising from the interaction between the chlorine used to bleach wood pulp and the organic extractives have been identified (Rogers and Keith 1974; Leach and Thakore 1975). One of these compounds, trichloroguaiacol, was identified in this study at a concentration below 10 $\mu g/\ell$ in the total effluent stream but was not detected in the plume beyond the discharge point. More sensitive analytical methods using an electron capture detector might reveal sub micrograms per litre levels in the effluent plume. Chlorinated phenols can cause tainting in fish at sub micrograms per litre levels (Shumway and Palensky 1973).

A number of monoterpene compounds associated with the turpentine fraction of the pulping process were identified but not quantified. These volatile compounds have been associated with fish tainting (Neil 1964) but were not found to persist beyond the immediate discharge area.

A high percentage of the total dissolved organic carbon present in the effluent occurred as compounds not observed in this study due to the selective nature of the extraction and analysis. These compounds presumably included those of high molecular weight and polymeric compounds such as large lignin breakdown fragments, wood sugars, starch, pectin and some compounds of very low molecular weight such as organo-sulphur compounds and methanol. With the exception of the organo-sulphur compounds, these compounds are not thought to have significant detrimental effects on the biota of the receiving waters.

Acknowledgments

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BROWNLEE, B., AND W. M. J. STRACHAN. 1977. Distribution of some organic compounds in the receiving waters of a kraft pulp and paper mill. J. Fish. Res. Board Can. 34. (This issue)

BUTTERY, R. E., R. M. SEIFERT, D. G. GUADAGNI, AND L. C. LING. 1971. Characterization of additional volatile components of tomato. J. Agric. Food Chem. 19: 524–529.

JUNK, G. A., ET AL. 1974. Use of macroreticular resins in the analysis of water for trace organic contaminants. J. Chromatogr. 99: 745–762.

LEACH, J. M., AND A. N. THAKORE. 1973. Identification of the constituents of kraft pulping effluent that are toxic to juvenile coho salmon (*Oncorhynchus kisutch*). J. Fish. Res. Board Can. 30: 479–484.

1975. Isolation and identification of constituents toxic to juvenile rainbow trout (*Salmo gairdneri*) in caustic extraction effluents from kraft pulp mill bleach plants. J. Fish Res. Board Can. 32: 1249–1257.

MORITA, M., H. NAKAMURA, AND S. MIMURA. 1974. Phthalic acid esters in water. Water Res. 8: 781–788.

NEIL, J. H. 1964. Report on the Spanish River, below the K.V.P. Company at Espanola. Ont. Water Res. Comm. Rep. 7 p.

POLAK, J., AND M. D. PALMER. 1977. Concentration pattern of chemical constituents in a paper mill's effluent plume: dynamics and model. J. Fish. Res. Board Can. 34. (This issue)

ROGERS, I. H. 1973. Isolation and chemical identification of toxic components of kraft mill wastes. Pulp Pap. Mag. Can. 74: T303–T308.

ROGERS, I. H., ET AL. 1975. Fish toxicants in kraft effluents. J. Tech. Assoc. Pulp Pap. Ind. 58: 136–140.

ROGERS, I. H., AND L. H. KEITH. 1974. Organochlorine compounds in kraft bleaching wastes. Identification of two chlorinated guaiacols. Fish. Mar. Serv. Res. Dev. Tech. Rep. 465: 21 p.

SHUMWAY, D. F., AND J. R. PALENSKY. 1973. Impairment of flavour of fish by water pollutants. U.S. Environ. Prot. Agency. EPA-R3-73-010.

THOMAS, N. A. 1973. Assessment of fish flesh tainting substances. Biological methods for the assessment of water quality. ASTM Am. Soc. Test. Mater. STP 528: 178–193.

Concentration Pattern of Chemical Constituents in a Paper Mill's Effluent Plume: Dynamics and Model[1]

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Polak, J., and M. D. Palmer. 1977. Concentration pattern of chemical constituents in a paper mill's effluent plume: dynamics and model. J. Fish. Res. Board Can. 34: 805–816.

The variation of conductivity in the effluent plume for a paper mill discharge on Lake Superior was studied to provide data for predictive models. The study included measurements of local winds and currents which were analyzed and related to the plume's location. To determine the spatial distribution of the plume, a statistical one-dimensional model relating plume conductivity and distance from the outfall and a two-dimensional phenomenological model assuming elliptically shaped isopleths were developed. It was found that chemical constituents of the plume can be expressed as linear functions of conductivity. The models thus enable the definition of the lake area affected by the effluent chemicals for different wind conditions.

Polak, J., and M. D. Palmer. 1977. Concentration pattern of chemical constituents in paper mill's effluent plume: dynamics and model. J. Fish. Res. Board Can. 34: 805–816.

Nous avons étudié la variation de conductivité dans la couche superficielle de l'effluent d'une papeterie dans le lac Supérieur afin d'obtenir des données pour des modèles prévisionnels. L'étude comprend des mesures des vents et courants locaux, qui ont été analysées et reliées à l'emplacement de la couche superficielle. Afin de déterminer la répartition spatiale de la couche superficielle, nous avons élaboré un modèle statistique à une dimension reliant la conductivité de la couche superficielle à la distance de l'émissaire et un modèle phénoménologique à deux dimensions supposant des isoplèthes de forme elliptique. Nous constatons que les constituants chimiques de la couche superficielle peuvent s'exprimer comme fonctions linéaires de la conductivité. Les modèles permettent donc de définir la région du lac affectée par les substances chimiques de l'effluent avec diverses conditions de vent.

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The dispersion of effluents discharged to the coastal regions of the Great Lakes is of interest to all concerned with water quality in these waters. These dispersion processes presently are analytically unsolvable; consequently most data available on dispersion have been obtained experimentally and reduced into statistical forms. Extensive dye dispersion and drogue tracking experiments have been carried out in both the oceans and fresh water, e.g. Okubo (1971), Pritchard and Carpenter (1960), Csanady (1970), Murthy and Csanady (1971), and Noble (1961). Most of these experiments have been conducted offshore although river dilution in estuaries has also received some attention. Recently, open channel discharges at the shore of large bodies of water have been studied as part of the environmental concern for cooling water discharges from power plants, and numerous references are available in the literature. All these studies defined dispersion as a function of time and/or space.

The wastewater effluent from the Domtar paper mill in Red Rock on Nipigon Bay of Lake Superior is discharged to the lake via an open channel (Fig. 1). The effluent plume was a focus of study on the lethal and sublethal (reproduction, disease, etc.) effects of toxicants on fish which required that mean concentrations of some of the discharged chemicals for the waters near the outfall be determined statistically. Some previous studies of the plume by Beak (1969) had indicated variability in the plume's concentration, dependence of plume orientation on the wind, and the effect of the shallow bay to the south of the discharge.

The objectives of our study were to establish a correlation between the concentration of various chemical components of a paper mill effluent and conductivity of the water, taking different wind conditions and current patterns into account, and

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

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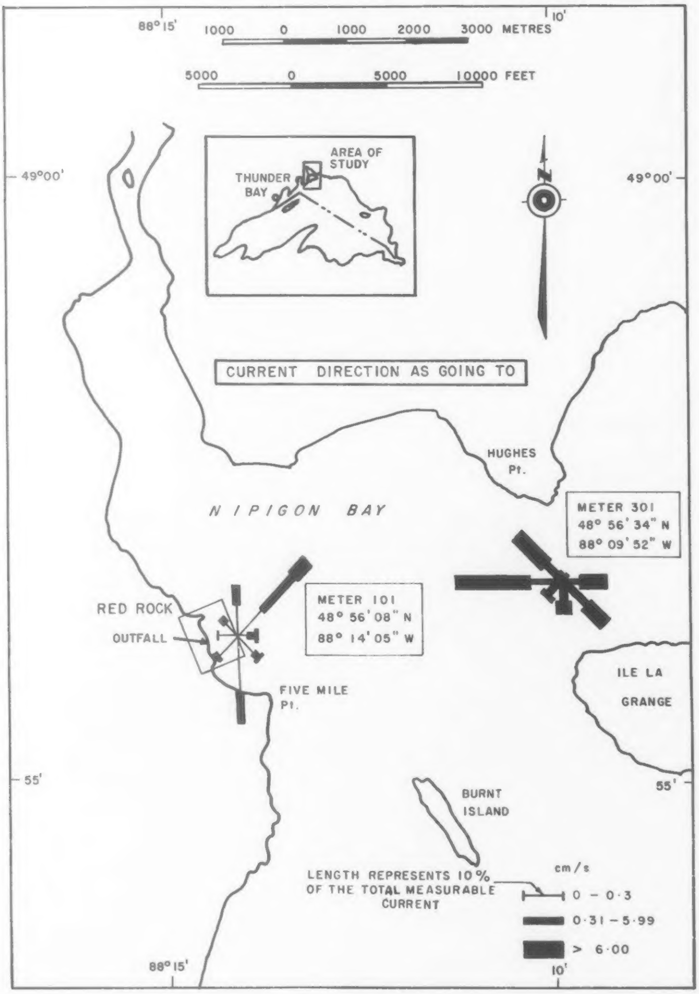
88°15'
10'
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49°00'
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AREA OF STUDY
THUNDER BAY
N
CURRENT DIRECTION AS GOING TO
HUGHES Pt.
N I P I G O N BAY
METER 301
48° 56' 34" N
88° 09' 52" W
METER 101
48° 56' 08" N
88° 14' 05" W
RED ROCK
OUTFALL
FIVE MILE Pt.
ILE LA GRANGE
55'
55'
BURNT ISLAND
LENGTH REPRESENTS 10% OF THE TOTAL MEASURABLE CURRENT
cm/s
0 – 0·3
0·31 – 5·99
> 6·00
88°15'
10'

FIG. 1. Nipigon Bay, Lake Superior, study area and currents in August 1974.

to construct a model to predict the conductivity pattern and hence the concentration pattern of other chemical constituents.

Materials and Methods

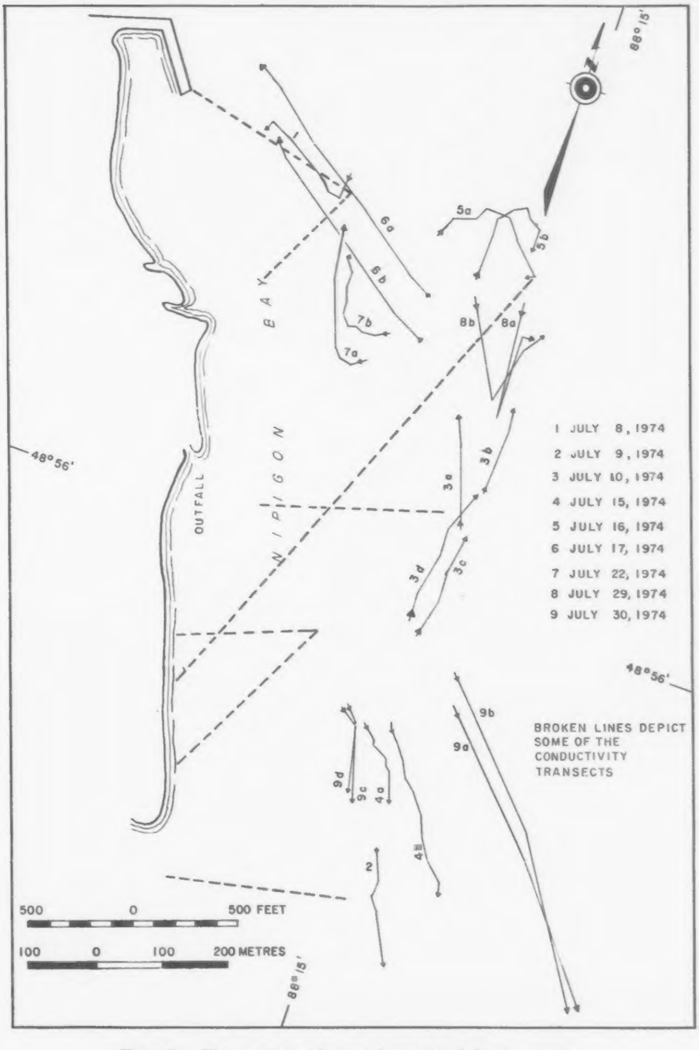
Most of the field measurements were made between June and September 1974 with some verification measurements in June 1975.

Statistically determining the properties of an effluent plume for nonconservative substances normally requires extensive laboratory analysis of samples. To reduce both the sampling and laboratory analysis requirements, the distribution of discharged substances in the plume was established by measuring conductivity profiles and collecting water volume samples at the same time.

Utilizing conductivity to identify the plume was based on the high values normally present in the effluent, relative ease of measurement, and the rapid response time of the probes.

PLUME CONDUCTIVITY

Conductivity of the plume was measured by a Lisle Instrument conductivity meter (results standardized to 25°C) equipped with a chart recorder. This meter was placed on a small boat and the plume was traversed with the conductivity probe kept at a constant depth from the lake surface. The start and end points of the transects were either at the moored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2 JULY 9, 1974
3 JULY 10, 1974
4 JULY 15, 1974
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6 JULY 17, 1974
7 JULY 22, 1974
8 JULY 29, 1974
9 JULY 30, 1974
48°56'
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2
BROKEN LINES DEPICT SOME OF THE CONDUCTIVITY TRANSECTS
500 0 500 FEET
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88°15'

FIG. 2. Drogue tracking and conductivity transects.

spar buoys surveyed in at the beginning of the survey or were determined for the individual runs using an optical fixing system and shore-based crew. A total of 9 transects were measured under northwest wind conditions and 15 for southeast wind conditions (Fig. 2). Each transect was measured twice, once with the conductivity probe near the lake surface, and the second time with the probe 1 m below the surface.

At some locations in the transect, samples for chemical analysis were taken. Chemical constituents and conductivity were determined for 180 samples, some of which analyses appeared in Polak (1975).

A conductivity function c_{tr} was used to show relative change of conductivity along the transect and defined as:

$$(1) \quad c_{tr} = (c - c_b)/(c_{max} - c_b)$$

where c is the conductivity at a given point, c_b the lake background conductivity (101 ± 13 μmhos/cm), and c_{max} the maximum conductivity along a given transect. The function c_{tr} varies between 0 and 1 with the 0 value outside the plume and 1 at the point where the conductivity is the maximum. The plume was highly variable both in space and time. The variability of the plume can be seen from comparison of two profiles obtained subsequently along the same transect (Fig. 3).

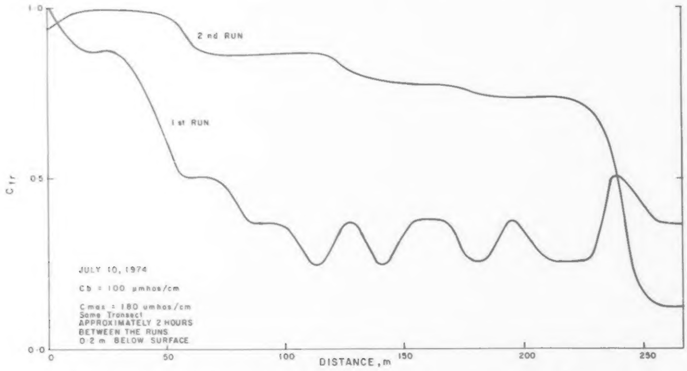

FIG. 3. Typical conductivity of a plume transect taken 2 h apart.

TABLE 1. Frequency of distribution of winds by direction (as %).

	Wind direction							
	N	NE	E	SE	S	SW	W	NW
Red Rock 1974 (June 22–Aug. 13)	24	0.7	0.3	35.5	18.0	4.0	3.6	13.7
Thunder Bay 1974 (June 27–Aug. 13)	11.4	22.1	11.3	6.4	3.7	20.3	13.1	11.3
Red Rock 1975 (June 4–July 12)	17.9	2.4	0.9	28.1	24.5	4.8	0.9	20.5

The outfall conductivity analog record for the period June 17–29, 1975 was digitized into a series of 290 hourly readings which had a mean value of 660.1 μmhos/cm and a standard deviation of 98.5 μmhos/cm. This record was numerically filtered using a moving average polynomial smoothing over five hourly readings, then analyzed for periodicities using standard time series analysis methods (Blackman 1965, chap. 10). The only significant period at the 80% confidence level was 24 h. This could be associated with some regular change in mill operation which resulted in the change in discharge concentration.

WINDS

To determine possible influence on the plume's position, on site wind measurements were made with a cup type recording wind anemometer (Lambrecht KG Type 1482) June 20 to August 13, 1974 and June 4 to July 12, 1975. These data are summarized in Table 1, with the complete data available in Polak (1974 and 1975). The winds at Red Rock are predominantly bidirectional (S and SE 53% and N and NW 38%). Although the wind data from the Thunder Bay airport are more evenly distributed with respect to direction, there is bidirectional tendency (E and NE 34.3% and W and SW 36.2%). If the measured winds at Thunder Bay are rotated clockwise 90° the frequency distributions are similar to those for Red Rock. The shift in ground wind direction at Red Rock is considered to be caused by local geomorphology with a line of high hills just west of Red Rock in a line approximately parallel to the shoreline. For the 1974 and 1975 summer data at Red Rock southeast winds occurred 1.4 times more frequently than northwest winds. Extending the Red Rock data using the Thunder Bay wind records for 1955–72 indicates that relatively calm conditions and winds other than those from the S and SE and W and NW occur on the average 20% of the time.

WATER MOVEMENTS

Concurrent with the measurement of conductivity profiles two types of water current studies were carried out at Red Rock. Drogue (Lagrangian) measurements were made to determine a general current pattern in the area, and Eulerian type measurements were made employing recording Savonius rotor current meters to obtain long-term statistical histories of currents.

Each drogue consisted of four aluminum panels (approximately 60 × 30 cm) joined together at right angles. The drogue was suspended from a small cylindrical styrofoam surface float marked with a colored flag for tracking purposes, submerged 1 m below the water surface, released, and tracked by optical triangulation using shore-based transits. The tracks are shown in Fig. 2 and summarized with

TABLE 2. Results of water movements in Red Rock at 1 m below water surface as determined by drogue tracking in July 1974. Drogue's locations are shown in Fig. 2. All drogues were 1 m below surface.

Date	Run	Resultant drogue speed (*cm/s*)	Resultant direction to (*degrees*)	Wind direction from	Wind speed (*m/s*)
July 8		3.48	279	SE	3.6
July 9		4.77	156	N	2.7
July 10	a	3.45	340	SE	1.3
	b	3.67	0		
	c	3.42	351		
	d	4.56	350		
July 15	a	2.06	143	N	3.1
	b	4.28	146		
July 16	a	2.71	96	SE	6.7
	b	1.88	46		
July 17	a	10.02	305	SE	4.5
	b	7.48	307		
July 22	a	2.97	332	SE	4.0
	b	1.98	320		
July 29	a	1.87	148	W	4.0
	b	4.36	81		
July 30	a	12.78	138		
	b	13.52	141		
	c	3.96	153	N	4.9
	d	3.55	159		

TABLE 3. Summary of results of water currents in Nipigon Bay, 1974. Currents were determined by Savonius rotor current meters at locations shown in Fig. 1.

	101		301		
Location	July	Aug.	July	Aug.	Sept.
Resultant speed (*cm/s*)	0.40	0.97	4.23	2.23	1.75
Result direction coming from (*degrees*)	173	237	111	87	69
Period of zero velocity (*% of recording time*)	58.4	52.5	0.0	4.61	6.95
Average speed (*cm/s*)	0.82	1.57	4.85	7.40	6.92
Maximum speed (*cm/s*)	7.72	20.0	10.61	28.68	30.80
Persistence	0.49	0.62	0.87	0.30	0.25
Number of readings	864	2160	288	4464	2229

wind data in Table 2. The current direction in the surface layer generally conformed to the wind direction.

Data on currents were gathered at two locations (Fig. 1) with Geodyne Model 102 current meters. One meter was located in the plume area 5.8 m below the surface in 11.9 m of water (location 101) and the other meter was moored midway between Hughes Point and Ile la Grange, 5.2 m below the surface in 11.6 m of water (location 301). Both meters recorded current magnitude and direction (averaged over 40 s) every 10 min. The meter in the plume area operated from July 25 to August 15, while the other meter functioned from July 29 to September 11, 1974.

As the purpose of this study was to determine long-term mean concentrations near the outfall, it was necessary to use the data gathered between June

TABLE 4. Significant spectral period (hours) of water currents in Nipigon Bay (80% confidence level).

Location and period	North–south component	East–west component
101 July 1974	2.6[a], 3.3, 6.0[a]	3[a], 3.2, 3.3[a]
101 Aug. 1974	2.2, 2.3, 2.5, 2.6, 2.8[a] 3.0[a], 3.2[a], 3.5, 4.0, 4.6, 5.0[a]	2.6, 2.7[a], 3.7, 4.1[a] 4.7[a], 5.7[a]
301 Aug. 1974	5.4, 6.3, 7.5, 10.9[a]	2.5, 2.6, 2.9, 5.4
301 Sept. 1974	2.5[a], 3.5, 5.2, 6.7[a], 12.0	5.7[a], 7.5

[a] 95% confidence level.

TABLE 5. Constituents and characteristics of Domtar (Red Rock) effluent Nipigon Bay. Data are based on samples taken during the morning shift on 6 different days in July 1974, and represent combined measurements of the three effluent streams.

		Combined stream	
Constituent	Unit	Mean	*SD*
Flow	m^3/d	96500	2400
Suspended solids	mg/ℓ	61.7	49.0
Dissolved solids	mg/ℓ	669.7	648.2
BOD	mg/ℓ	213.5	182.0
COD	mg/ℓ	462.7	491.6
Conductivity at 25°C	μmhos/cm	601.6	395.7
Turbidity	Formazin Unit	27.9	19.0
pH	—	8.26	1.41
Alkalinity	$CaCO_3$ mg/ℓ	173.5	131.4
Sodium	mg/ℓ	134.5	143.3
Potassium	mg/ℓ	7.48	7.48
Chloride	Cl mg/ℓ	59.6	95.5
Sulphate	SO_4 mg/ℓ	140.6	123.2
Phenols	phenolic equiv. μg/ℓ	700.0	647.2

and September to predict concentrations expected during the rest of the year. This was done in three stages. The plume data were related to wind data recorded at Red Rock. Then the Red Rock wind records were statistically related to the long-term wind statistics available at the Thunder Bay Airport. Finally, measured currents at Red Rock were related to wind data. Unfortunately, it was not possible to operate recording current meters near the water surface where the plume was found to be located; consequently the last stage was only a qualitative check as the currents are also depth dependent.

A summary of data for currents is presented in Table 3 with the complete data available in Polak (1974). The current frequency roses for August 1974 are shown in Fig. 1. The resultant current at location 101 (near the effluent plume) is in a NNE direction with a magnitude of 0.7 cm/s while at location 301 the resultant is westerly with a magnitude of 2.7 cm/s. This demonstrates the differences in water movements between the western and eastern shores of Nipigon Bay. A time series analysis (Blackman 1965) of the data revealed the strong influence of Lake Superior water level oscillations on water movements in Nipigon Bay. The statistically significant periodicities appear in Table 4.

Development of a One-Dimensional Model

In this section, a method for prediction of the dilution of the plume based on conductivity data is developed. The conductivity results are then compared to other chemical measurements.

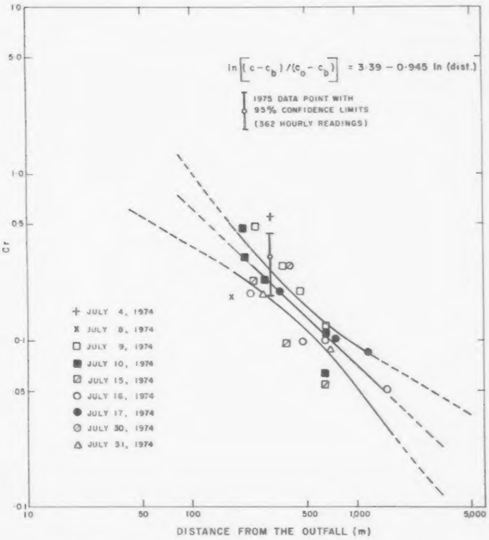

FIG. 4. Dependence of c_r on the distance from the outfall.

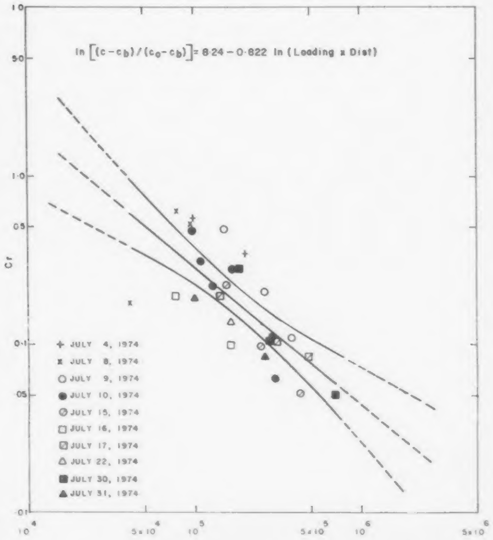

FIG. 5. Dependence of c_r on the distance × loadings.

Details of the flow and chemical composition of the three effluent streams as determined by sampling in July 1974 appear in Polak (1974). Total discharge flow varied little, while concentration sometimes varied by an order of magnitude (Table 5). To relate conductivity of the plume with that of the effluent, the effluent conductivity was continuously monitored by a recording conductivity meter. Recorded conductivity varied between 400 and 950 μmhos/cm, with changes of a few hundred μmhos/cm in several hours not uncommon.

Next the dependence of relative conductivity on distance from the outfall and the dissolved solids loadings for the mill effluent were determined. Loadings were estimated from records of the total discharge and its conductivity, assuming the conductivity (μmhos/cm) × 0.65 = dissolved solids (mg/ℓ). The relative conductivity c_r was defined as:

$$(2) \quad c_r = (c - c_b)/(c_o - c_b)$$

where c is the mean conductivity of the transect through the plume at a given distance from the outfall, c_o the conductivity of the outfall and c_b lake background conductivity. Relative conductivity depended on distance from the outfall and dissolved solid loading (Fig. 4 and 5). Including the loading data in the fitting (Fig. 5) did not reduce the confidence bands shown in Fig. 4. Possibly the variability of other factors masked the discharge variation. Statistical fitting of the data does not have an intercept of $c_r = 1.0$ at a distance of zero. Consequently it is necessary to assume some virtual origin which is greater than unity that is due to initial mixing processes (Hinze 1959, p. 337). The fitted variables have dimensions which affect the general applicability of the results. Efforts to evolve a meaningful dimensionless distance variable were unsuccessful.

Coefficients for the linear equation correlating logarithms of relative conductivity and the distance from the outfall (or distance × loadings) were significant at the 90% confidence level (Table 6). Here the data sets were divided according to the prevalent wind directions at the time of measurement and the coefficients calculated for each wind condition.

In 1975, measurements were carried out to improve the prediction of the one-dimensional spread of the plume. Two recording conductivity meters were located first in approximately a north–south direction at 300 and 1000 m from the outfall to record the spread of the plume along the shore. Later on, the same meters were moored in the east–west direction at distances of 200 and 800 m. Unfortunately, only one meter in the north–south direction 300 m from the outfall recorded meaningful data from June 18 to July 4, 1975. From these data reduced conductivities c_r were computed (Table 7).

The mean value for the recording conductivity meter is slightly above the correlation line calculated from the 1974 survey; however, the 95% confidence intervals of the point and prediction

TABLE 6. Dependence of the relative conductivity on the distance from the outfall and loadings.

Main wind direction	Range from outfall (m)		Coefficients of the Equation $\ln(c_r) = a + b\ln(x)$			Correlation coefficients
	From	To	a	b	x	
NW	240	1500	5.24	1.16	distance from the outfall (m)	−0.796
SE	180	1160	2.95	0.796		−0.783
All winds	180	1500	3.39	0.945		−0.775
NW	240	1500	12.75	1.18	(distance from outfall × diss. solids loadings) ($g\ s^{-1}\ m$)	−0.834
SE	180	1160	6.92	0.719		−0.674
All winds	180	1500	8.24	0.822		−0.723

TABLE 7. Results of c_r determined June 18 to July 4, 1975. Meter located 300 m southeast of the outfall.

Winds from	Mean c_r	SD	No. of hourly readings
N + NW	0.301	0.060	94
S + SE	0.324	0.061	224
Other winds	0.319	0.061	362

line overlap (Fig. 4). Although the single data point improves the confidence in the fitted line, it is insufficient to improve the statistics of the predictive line or to extend the range of predictions.

In the approach presented in the foregoing, a circular symmetry of the plume was assumed. Observations of the plume indicate it spreads predominantly along the shore due to the location of the outfall, currents in the area, and the confining properties of the floating wood scum boom installed at the outfall; consequently, a simple two-dimensional model was developed.

Two-Dimensional Spread of the Plume

The two-dimensional model uses also the relative concentration of the plume c_r defined by equation (2).

This model is based on two assumptions: (a) c_r is decreasing exponentially with increasing distance from the outfall and, (b) the isopleths connecting the constant c_r values are elliptical in shape centered on the outfall. The first assumption can be expressed as:

$$(4)\quad c_r = e^{-k_1 b}$$

where b is the distance to the middle of the plume from the outfall and k_1 is a constant, and the second condition expressed as:

$$(5)\quad p^2/a^2 + q^2/b^2 = 1$$

which is the equation of an ellipse in the p–q Cartesian coordinate system (Fig. 6). Combining equations (4) and (5) and transforming to a x–y Cartesian coordinate system, the equation for c_r is:

$$(6)\quad c_r = \exp\left(-k_1\sqrt{(y\cos\alpha - x\sin\alpha)^2 k_2^2 + (x\cos\alpha + y\sin\alpha)^2}\right)$$

where k_1 relates the concentration decrease with the distance from the outfall, k_2 is the ratio of the two axes of the ellipse and α the angle between the major axis of the ellipse and the x axis. The coefficients k_1, k_2, and α were calculated by a modified Newton–Raphson method using all available data to calculate the step increments by a least-square method (Polak and Lu 1972).

For each plume transect the end and quarter points along with the middle and maximum concentration point were used as input data. The statistically evaluated coefficients for different wind conditions and depth appear in Table 8. These coefficients were used to calculate the smooth isopleths for $c_r = 0.8$, 0.4, 0.2, and 0.01 (Fig. 7 and 8) where $c_r = 0.01$ is assumed to be the limit of the plume. For simplicity, the confidence bands are only shown in Fig. 6. Similar bands apply for Fig. 7 and 8.

The isopleths for the surface are located further away from the outfall than those 1 m below surface, showing that the plume spreads mainly near the lake surface. Comparing the plume predictions for NW (Fig. 7) and SE (Fig. 8), one observes that the main direction of the plume does not change by as much as one would expect. Perhaps the limited data, experimental errors, and short duration changes of winds, currents and plume positions are not properly represented in this simplified model. However, for SE

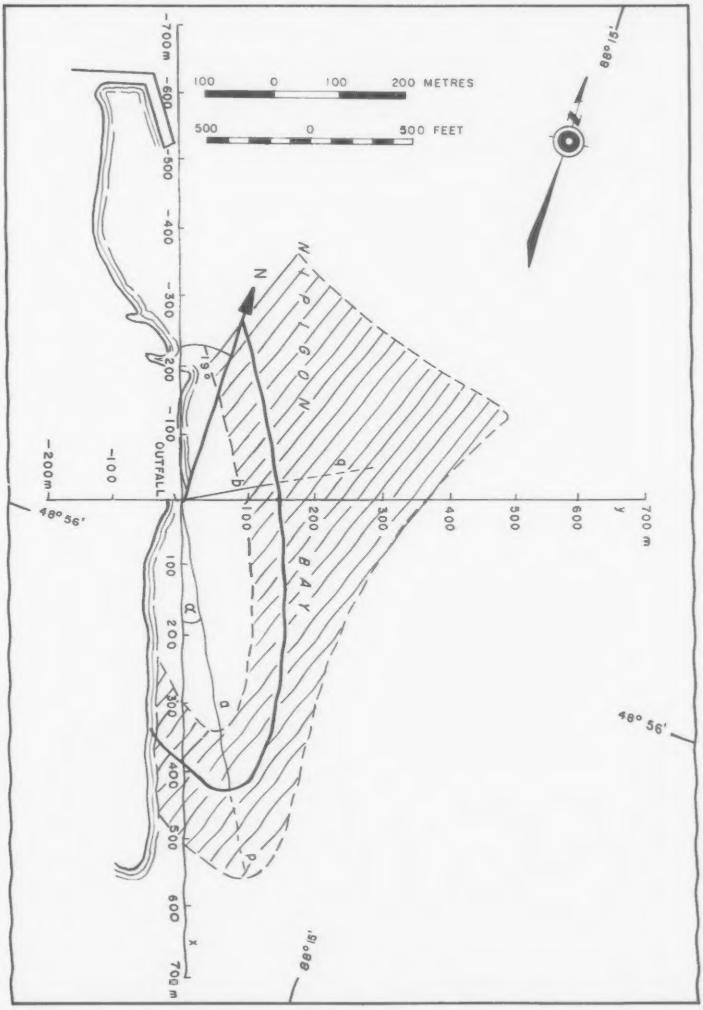
100 0 100 200 METRES
500 0 500 FEET
N
NIPIGON BAY
OUTFALL
48° 56'
88° 15'
19°
-700 m
-600
-500
-400
-300
-200
-100
-200 m
100
200
300
400
500
600
700 m
x
y
a
b
α
d

FIG. 6. Coordinate system and 95% confidence level band of the two-dimensional model.

winds, the plume does spread farther from the outfall and the shore than for the NW wind conditions, particularly for the surface plume. Thus, the two-dimensional model matches the field observations more closely than the one-dimensional model and differentiates the two wind conditions which the one-dimensional model failed to do.

PLUME CONSTITUENTS OTHER THAN CONDUCTIVITY

Evaluation of the parameters of equation (6) for constituents other than conductivity using results of analysis of volume samples collected was not possible because exact location of many of the samples was not shown. Instead, the different sample constituents were statistically correlated with sample conductivity (Table 9). The best correlations of plume constituents with conductivity in statistical order of significance were BOD, dissolved solids, and COD, respectively. This is surprising as BOD and COD are both nonconservative contaminants being provided oxygen from the lake water during transport in the

TABLE 8. Numerical values of coefficients of equation defining two-dimensional spread of the plume (equation 6) for different wind conditions and depths.

Prevalent wind direction	Depth below surface (*m*)	Calculated coefficients and their variances					
		k_1	σ_{k1}^2	k_2	σ_{k2}^2	α	σ_α^2
NW	0.2	0.00362	1.9×10^{-7}	3.16	0.364	8.69	7.06
NW	1.0	0.00629	1.8×10^{-6}	4.10	1.66	−1.45	9.98
SE	0.2	0.00241	1.1×10^{-7}	3.97	0.156	7.29	2.14
SE	1.0	0.00377	2.8×10^{-7}	3.72	0.160	−1.51	2.91

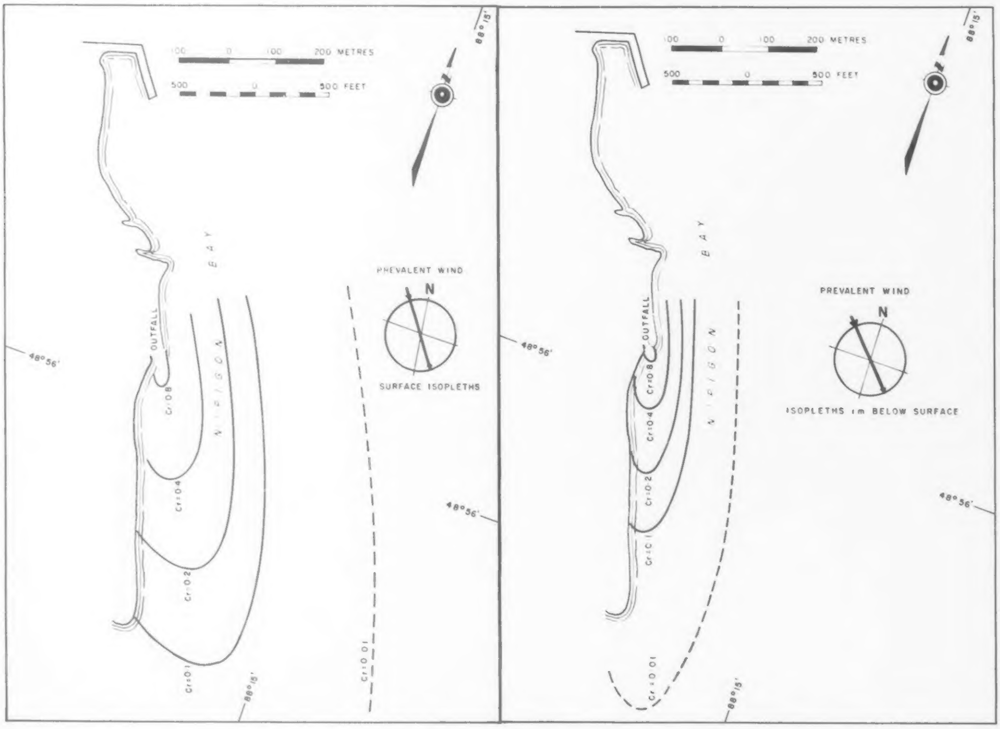

FIG. 7. Calculated c_r isopleths for NW winds.

plume. However, as all the samples were collected relatively close to the outfall, the time lag (1.4–13.8 h) between discharge and sampling is too short for a significant degradation to be detectable. It is therefore possible to assume that BOD, dissolved solids and COD show a pattern similar to that of conductivity, and using the coefficients from Table 9, concentration plumes similar to those shown for conductivity (Fig. 7 and 8) can be drawn.

The statistical fitting of effluent plume concentrations for winds parallel to shore does permit prediction of what percentage of the year various concentrations of discharge can be expected. The statistical technique also quantifies the variation for these concentrations. Unfortunately a meaningful dimensionless parameter could not be evolved for the statistical model fitting so that the results are not readily transferable to other lake sites, although one expects discharges at the shore will dilute in a similar manner for other locations.

TABLE 9. Correlation between conductivity and other chemical constituents.

Constituent (p)	m from surface	No. of samples	Coefficients of equation $p = a \times$ conductivity (μmhos/cm) $+ b$: a	b	Correlation coefficient (r)
Suspended	0.2	94	0.182	−19.3	0.554
solids mg/ℓ	1.0	65	−0.0342	21.1	−0.041
Dissolved	0.2	94	1.110	−61.3	0.946
solids mg/ℓ	1.0	64	0.979	−36.3	0.814
BOD	0.2	89	0.291	−37.1	0.961
mg/ℓ	1.0	64	0.309	−40.6	0.930
COD	0.2	92	0.671	−67.5	0.946
mg/ℓ	1.0	65	0.551	−52.6	0.734
Sodium as	0.2	97	0.175	−18.4	0.872
Na mg/ℓ	1.0	64	0.165	−14.8	0.355
Potassium as	0.2	95	0.00773	−0.7016	0.919
K mg/ℓ	1.0	65	0.00642	0.0867	0.814
Chlorides as	0.2	92	0.0849	−11.2	0.805
Cl mg/ℓ	1.0	65	0.0571	−5.94	0.578
Sulphate as	0.2	92	0.226	−25.1	0.880
SO_4 mg/ℓ	1.0	65	0.194	−20.9	0.859
Phenols as	0.2	88	0.764	−67.3	0.611
phenolic equiv. μg/ℓ	1.0	60	0.850	−92.9	0.724

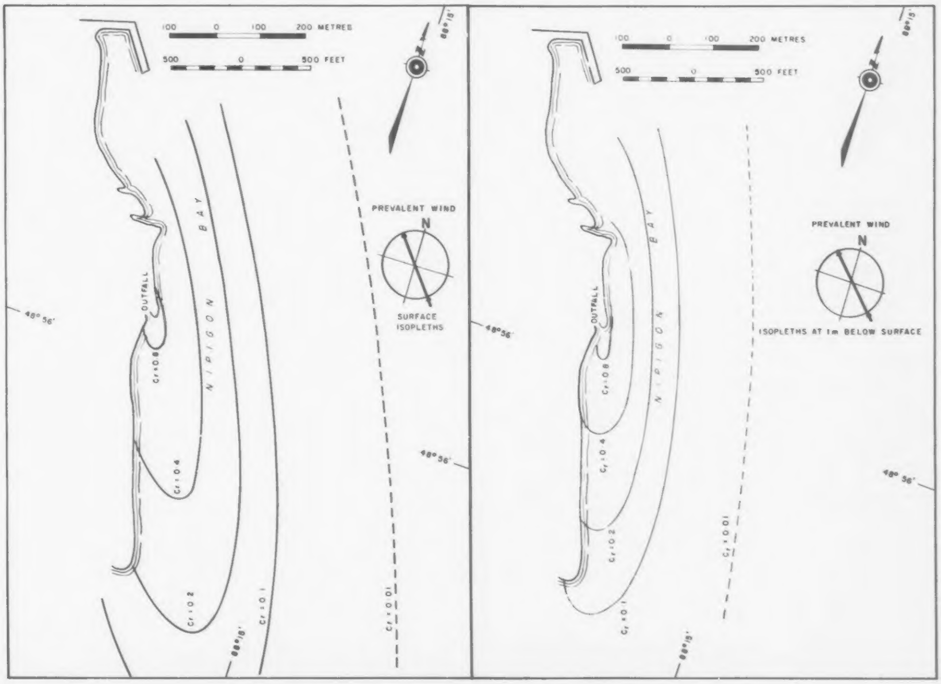
100 0 100 200 METRES
500 0 500 FEET
88°15'
PREVALENT WIND
N
SURFACE ISOPLETHS
ISOPLETHS AT 1m BELOW SURFACE
NIPIGON BAY
OUTFALL
48°56'
Cr = 0.8
Cr = 0.4
Cr = 0.2
Cr = 0.1
Cr = 0.01

FIG. 8. Calculated c_r isopleths for SE winds.

Acknowledgments

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Beak, T. W. 1969. Domtar Newsprint Ltd., Red Rock mill pollution abatement program. Beak Consultants Limited, Mississauga, Ont. 42 p.

Blackman, R. B. 1965. Linear data-smoothing and prediction in theory and practice. Addison-Wesley Publishing Co. Inc., Reading, Mass. 182 p.

Csanady, G. T. 1970. Dispersal of effluents in the Great Lakes. Water Res. 4: 79–114.

Hinze, J. O. 1959. Turbulence, an introduction to its mechanism and theory. McGraw-Hill Book Co., New York, N.Y., 568 p.

Murthy, C. R., and G. T. Csanady. 1971. Experimental studies of relative diffusion in Lake Huron. J. Phys. Oceanogr. 1: 17–24.

Noble, J. E. 1961. Measurement of horizontal diffusion in the Great Lakes. Proc. Conf. Great Lakes Res. 10: 85–95.

Okubo, A. 1971. Oceanic diffusion diagrams. Deep-Sea Res. 18: 789–802.

Polak, J. 1974. Red Rock–Domtar effluent plume chemistry. Ontario Ministry of the Environment, Toronto, Ontario, 62 p.

1975. Red Rock–Domtar effluent plume chemistry, 1975 update. Ontario Ministry of the Environment, Toronto, Ontario, 14 p.

Polak, J., and B. C. Y. Lu. 1972. Second virial coefficients of polar gases. A correlation with Stockmayer potential function. Can. J. Chem. Eng. 50: 553–556.

Pritchard, D. W., and J. H. Carpenter. 1960. Measurements of turbulent diffusion in estuarine and inshore waters. Bull. Int. Assoc. Sci. Hydrol. No. 20: p. 37–50.

Effect of Pulp Mill Effluent on the Surficial Sediments of Western Nipigon Bay, Lake Superior[1]

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SANDILANDS, R. G. 1977. Effect of pulp mill effluent on the surficial sediments of western Nipigon Bay, Lake Superior. J. Fish. Res. Board Can. 34: 817–823.

Bottom sediment samples were obtained in June 1974 to determine the zone of influence of a point source discharge from the kraft paper mill at Red Rock, Ont. The composition of the samples were described by particle-size distribution, organic and inorganic carbon, major elements and trace element analyses. Correlation coefficients and cluster analysis were used to determine any characteristic associations. The results showed that the mill discharge decreased pH and increased organic matter in the sediment. Above average concentrations of total sulphur and mercury appeared to be associated with this organic matter. These effects were localized around the point source (1.5 km) and were detectable to about 5 km downstream from the mill outfall.

SANDILANDS, R. G. 1977. Effect of pulp mill effluent on the surficial sediments of western Nipigon Bay, Lake Superior. J. Fish. Res. Board Can. 34: 817–823.

Nous avons prélevé en juin 1974 des échantillons de sédiment benthique afin de déterminer la zone d'influence d'une source ponctuelle d'effluent de l'usine de papier draft à Red Rock, Ont. Nous décrivons la composition des échantillons selon la distribution de la grosseur des particules, le carbone organique et inorganique, les éléments majeurs et les analyses d'oligoéléments. Les coefficients de corrélation et l'analyse des groupements ont servi à déterminer toute association de caractéristiques. Les résultats démontrent que l'effluent du moulin diminue le pH et augmente la matière organique dans le sédiment. Des concentrations dépassant la moyenne de soufre total et de mercure semblent être associées à cette matière organique. Ces effets sont localisés autour de la source ponctuelle (1.5 km) et sont détectables jusqu'à environ 5 km en aval de l'émissaire de moulin.

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A limited number of studies have been published on the major element geochemistry of the Upper Great Lakes. The most detailed have been carried out in Lake Superior by Nussman (1965), in Lakes Superior and Michigan by Callender (1969), and in southern Lake Michigan by Shimp et al. (1971). The primary use of major element analyses in sediment geochemistry is to indicate the predominant mineral phases present and to provide some insight into sediment dispersal. This may form a mineralogical base for interpreting how trace elements and other components may be bound in the sediment (Sly and Thomas 1974).

This approach has been used to examine the sediments of western Nipigon Bay and to determine how they are affected by the wastewater discharged from the kraft paper mill at Red Rock, Ont. Previously reported data on the surficial materials of Nipigon Bay (Mothersill and Fung 1972) were based on a grid of widely spaced samples and provided only a general background to the geochemistry of the area.

In this study the sample locations were chosen specifically to show the extent of the pulp mill discharge and its influence on bottom sediment materials (Sandilands 1975).

General Description of the Study Area

The Nipigon River drains approximately 25,000 km^2 of the Canadian Shield, including Lake Nipigon. In 1972, the mean discharge of the river was reported at 420 m^3·s^{-1} (Water Survey of Canada 1972). South of the townsite of Nipigon, the river widens to form Nipigon Bay (Fig. 1) which extends about 16 km south and 40 km east of the river mouth. The western

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

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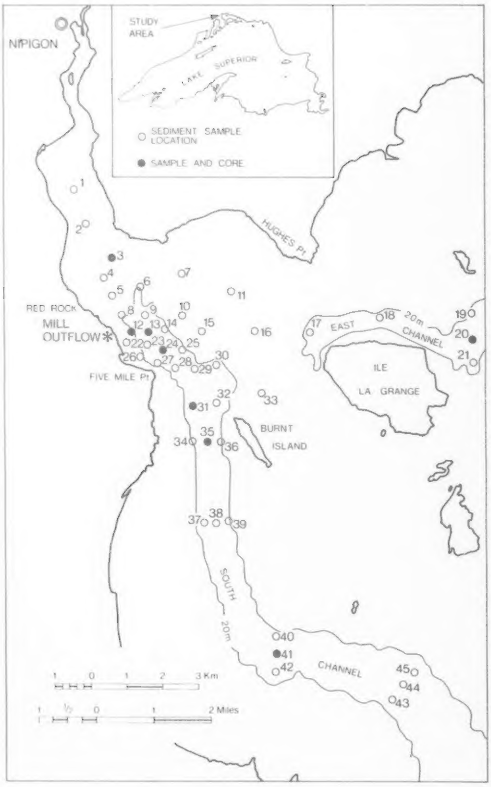


FIG. 1. Sediment sample locations in western Nipigon Bay.

part of the Bay is divided into two channels. The south channel runs between Five Mile Point and Burnt Island and then parallels the western shoreline until it enters Lake Superior through the Nipigon Straits. The east channel runs parallel to the north shore between Hughes Point and Ile la Grange and then into the eastern half of the bay.

Near its mouth, the Nipigon River cuts through erosional remnants of a thick sheet or sill of diabase, which overlies either flat lying sedimentary rock of the Sibley Series or in places, Algoman granitic rocks. The Sibley Series, red, due to the presence of small amounts of hematite, consists of shales, shaley dolomites, and dolomitic limestone with interbedded sandstone (Pye 1962). The bedrock is overlain by calcareous varved clays and tills (Zoltai 1965).

At the northwestern end of Nipigon Bay, a large paper mill at Red Rock, discharges about 96,000 m^3/day of wastewater effluent into the bay (average flows in July 1974 as reported by Polak and Palmer [1977]). This effluent contained an average of 6.51 t/day of suspended solids. T. W. Beak Consultants (1969) reported an average suspended solids loading of approximately 47 t/day in 1969 before plant modifications.

Methods

Trace metals and organic matter show a preferred occurrence with fine grained (< 16 μm) sediment (Thomas 1972, 1973; Allersma and de Groot 1974) and may indicate the areas influenced by paper mill effluent. Therefore, sediment samples were concentrated around the mill and in deep water regions of likely fine sediment accumulation. Samples were collected (Fig. 1) on June 24–26, 1974, at predetermined locations by dead reckoning from marker buoys and prominent landmarks and by comparison of echo sounder depths with those given on the Canadian Hydrographic Service Chart 2312. Forty-five bottom samples and eight cores (up to 60 cm in length) were obtained using a ponar grab sampler and a phleger corer (Sly 1969). Temperature, Eh and pH values were measured from within the top 1.5 cm of the grab sample and then the top 1 cm was subsampled.

One subsample was frozen and later freeze-dried and lightly ground. The concentrations of the following major elements: Si, Al, K, Na, Mn, Fe, Ca, Mg, S, P. Ti, were determined from the ground sample by X-ray fluorescence using a Phillips P.W. 1220 C automatic spectrometer (Thomas et al. 1972). The percentage organic and inorganic carbon was determined using a Leco induction furnace carbon analyzer and sulphurous acid digestion at room temperature (Kemp et al. 1972). The trace elements Ni, Pb, Cu, and Cr were determined on a Techtron AA-5 atomic absorption spectrophotometer after hot concentrated HC1 extraction. Mercury was analyzed using flameless atomic absorption after acid extraction (Thomas 1972). All element concentrations are expressed relative to the dry weight of sediment.

Another sediment subsample was retained wet and particle size distribution was determined using a Micromeritics sedigraph 5000 analyzer (Duncan and Rukavina 1972). Coarse organic material and clumping of organic fibers, which blocked the flow, prevented the size analysis of seven samples. These samples were located close to the mill outfall. A computer program (Rukavina and Dolling 1973) was used to process the sedigraph results to provide the percentage size composition and moment measures.

The geochemical results were evaluated in a computer program (Cameron 1967) to generate a linear correlation coefficient matrix (Table 1) of 18 variables using 43 sample points. Two samples, 12 and 22, were omitted from the statistical analysis since they had anomalously high organic values and missing data. For a 95% confidence level, the critical value for the coefficient of correlation is 0.304 for 43 samples (Freund 1970).

A cluster dendrogram is presented in an attempt to show relationships of the variables and the sample similarities. All 26 variables were evaluated using a simple cluster analysis program (Davis 1973) which used a technique of weighted pair–group method with arithmetic averages. The features of this method are:

1) the correlation coefficient is used as a similarity measure;

2) highest similarities are clustered or linked first;

3) two objects can be connected only if they have mutually highest correlation with each other;

4) after two objects are clustered, their correlations with all other objects are averaged.

It should be noted that the procedures in #4 above will introduce a distortion as successive levels of clusters are averaged together. This program was used to cluster the sample stations (Fig. 4) and variables (Fig. 5).

Results

PHYSICAL CHARACTERISTICS

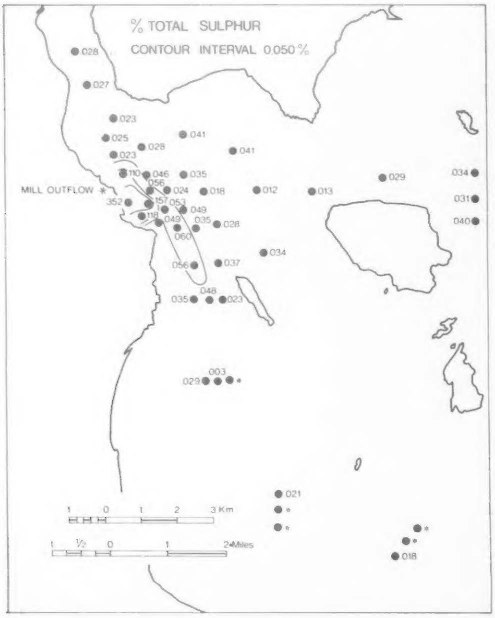
Most grab samples consisted of a thin (0.5–1.0 cm) oxidized surface layer of brown mud overlying structureless grey mud. Near the river mouth, mean sediment size was approximately 8 μm (7 phi) and averaged about 65% silt-size and 35% clay-size material. The samples farthest from the river mouth in both channels had a mean size of approximately 3–4 μm (8.25 phi) and contained about 40% silt-size and 60% clay-size material. The redox potential (Eh) of the sediment samples showed no apparent pattern or correlation with other factors. At most locations, Eh values were below +0.200V, suggesting a reducing environment. The hydrogen ion concentration (pH) ranged from 5.3 to 7.3, with values less than 6.0 at all stations within 1 km of the point source. It was also noted that the organic content was high at these locations. Organic fibers were visible in all bottom samples within 1.5 km of the outfall. Bark and/or wood chips were found in the top 10 cm of most samples within 6 km of the outfall. The cores generally were similar to the surface samples, consisting of structureless recent muds. However, at station 35, the core penetrated through a thin layer of mud into glacial sediments and at station 12, the core consisted of 30 cm of coarse organic material over mud.

CHEMICAL CHARACTERISTICS

The concentration of all the major elements, with the exception of total-S, was fairly uniform throughout the area. Most of the elements showed a decrease in concentration near the outfall, due to the dilution of the inorganic fraction by the increasing amounts of organic material. The strong correlation of Fe with Ti (0.908) (Table 1) suggests the presence of ilmenite and/or rutile whereas the Al to Fe correlation (0.910) indicates that the iron compounds are probably bound to the clay minerals (Sly and Thomas 1974). In addition, the correlation of K with clay (0.918) and K with Al (0.944) suggest the predominance

TABLE 1. Correlation coefficients of chemical parameters from 43 sediment samples. (*Significant at .05 level, **Significant at .01 level).

	Al	Mg	Ca	Na	K	Ti	P	Mn	S	Fe	Cr	Cu	Ni	Pb	OC	IC	Hg
Si	.611**	.350*	.020	.834**	.553**	.185	−.058	.434**	−.769**	.305*	.161	−.315*	.321*	.430**	−.847**	−.225	−.566**
Al		.344*	−.632**	.754**	.944**	.782**	−.035	.724**	−.691**	.910**	.452**	.230	.698**	.823**	−.747**	−.601**	−.155
Mg			.224	.583**	.306*	.140	.627**	.021	−.554**	.324*	.151	.023	.458**	.227	−.532**	.290	−.260
Ca				−.025	−.669**	−.742**	.448**	−.558**	−.028	−.741**	−.408**	−.608**	−.404**	−.672**	.033	.840**	−.272
Na					.696**	.315*	.214	.472**	−.888**	.521**	.192	−.157	.518**	.561**	−.879**	−.133	−.403**
K						.641**	−.079	.719**	−.571**	.852**	.440**	.424**	.660**	.926**	−.608**	−.573**	−.081
Ti							−.115	.631**	−.368*	.908**	.520**	.216	.625**	.525**	−.484**	−.701**	−.039
P								−.146	−.277	.022	−.056	−.055	.176	−.136	−.164	.517**	−.166
Mn									−.439**	.699**	.383*	.092	.530**	.646**	−.547**	−.603**	−.258
S										−.511**	−.257	.309*	−.546**	−.429**	.921**	.106	.481**
Fe											.527**	.354*	.738**	.755**	−.569**	−.629**	−.092
Cr												.246	.828**	.360*	−.331*	−.466**	−.196
Cu													.224	.523**	.359*	−.319*	.396**
Ni														.546**	−.582**	−.399**	−.432**
Pb															−.441**	−.531**	−.140
OC (organic carbon)																.205	.505**
IC (inorganic carbon)																	−.097


% TOTAL SULPHUR
CONTOUR INTERVAL 0.050 %
MILL OUTFLOW *
.028
.027
.023
.025
.028
.023
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110
.046
.035
056
.024
.018
.012
.013
.029
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.031
.040
352
157
053
.049
118
.049
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.028
060
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056
.037
048
035
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003
029
*
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.018
1 0 1 2 3 Km
1 ½ 0 1 2 Miles

FIG. 2. Distribution of total-S in surficial sediment samples in percent dry weight of sediment (* — undetectable).

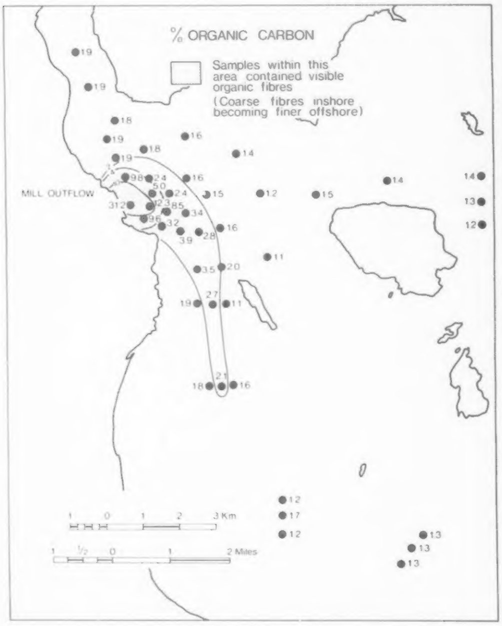
% ORGANIC CARBON
Samples within this area contained visible organic fibres
(Coarse fibres inshore becoming finer offshore)
MILL OUTFLOW
19
19
18
19
18
16
14
19
98
24
16
50
24
15
12
15
14
14
13
12
312
123
85
34
96
32
16
39
28
11
3.5
20
27
19
11
21
18
16
12
17
12
13
13
13
1 0 1 2 3 Km
1 ½ 0 1 2 Miles

FIG. 3. Distribution of organic C in surficial sediment samples in percent dry weight of sediment.

of illite with only minor amounts of chlorite (Mg to Al, $r = 0.344$). Analysis of core subsamples (5-cm long subsections) showed similar strong correlation of Al with K (0.925) and Fe with Ti (0.944).

Total-S in grab samples (Fig. 2) ranged from undetectable amounts in the south channel to 0.35% at station 22 and showed a direct correlation with proximity to the mill outfall. The organic carbon (Fig. 3), with an average of 1.5–2.0% in the river mouth and in both channels, also increased towards the outfall, and reached 31% at station 22. Organic carbon and total-S correlated strongly, with $r = 0.921$ (Table 1), and both showed a positive correlation with Hg (.505 and .481, respectively). Total-S was detectable only in the top subsample of cores 3, 12, 13, 20, and 31 and is probably related to the occurrence of organic material. However, in cores 24, 35, and 41, total-S levels averaged about 0.05% throughout the entire core and may indicate the presence of sulphides rather than a relationship with organic matter.

The concentration of the trace elements Cu, Ni, and Pb were fairly uniform across the area, ranging from 29 to 41, 6 to 69, and 11 to 42 μg/g, respectively. Cr had a greater range (11–132 μg/g, and variation. Cr and Ni correlated strongly ($r = 0.828$) and showed secondary relationship to the elements associated with clay minerals (Fe, Ti, Al, K). Pb correlated strongly with K (0.926) and Al (0.823) and suggests an association with illite. Cu correlated with Pb and K and weakly with Hg and organic carbon.

Hg ranged from 30 to 420 ng/g and also increased with proximity to the outfall with the highest value at station 13. Hg averaged 50 ng/g in the river mouth samples, 130 ng/g in the east channel samples, and 110 ng/g in the south channel samples. The core at station 13 had 360 ng/g in the top subsample (0–5 cm) while the rest of the core was near background levels with an average of 80 ng/g. As mentioned earlier, there is a correlation with organic carbon, total-S, and Cu (Table 1).

CLUSTERING

The output (Fig. 4) from the cluster analysis of 43 sample stations shows five major clusters or groupings. By comparing the sample numbers in each group with their locations (Fig. 1), it can be seen that the clusters represent five major zones or environments of the study area (river mouth, near mill outfall, northeast fringe, east channel, and south channel). The analytical data are summarized by mean and standard deviation (Table 2) for each of these five zones. These

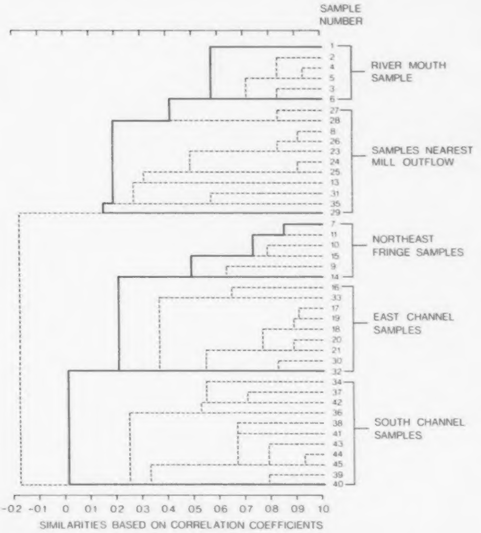

FIG. 4. Q-mode cluster dendrogram prepared by the weighted pair–group method using arithmetic averages (Davis 1973).

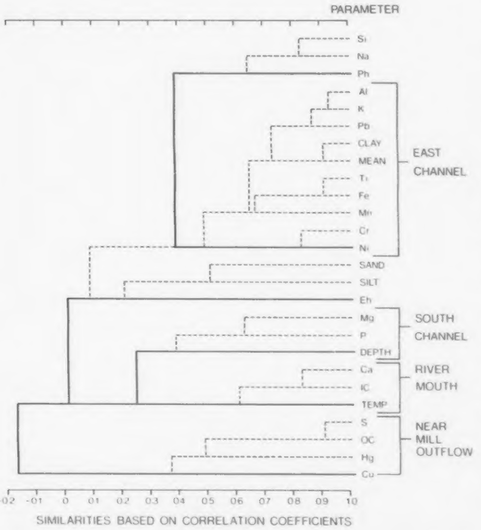

FIG. 5. R-mode cluster dendrogram prepared by the weighted pair–group method using arithmetic averages (Davis 1973).

means were used to determine if there is a significant relationship between the groupings of variables or cluster facies (Fig. 5) and the five zones (Fig. 4).

The river mouth samples had the highest values for Ca and inorganic carbon, while Mg and P were highest in samples from the south channel. These two clusters together formed a carbonate cluster facies associated with the river input.

The variables in the cluster associated with clay minerals had their highest values in the east channel samples and this cluster facies was considered to be the characteristic association for this zone.

The variables in the S, OC, Hg cluster facies had their highest values in samples near the mill outfall and (as mentioned earlier), are characteristic of the effects of the mill discharge on the sediments.

The remaining clusters of variables (Na, Si, pH and sand, silt, Eh) did not seem to be associated with any specific zone. In addition, the northeast fringe zone may only represent a transition zone between river mouth, near mill and east channel samples.

Discussion

Current measurements (Polak and Palmer 1977) indicated that currents near the outfall generally travelled along the shore. In the east channel, between Hughes Pt. and Ile la Grange, the current was stronger, mainly in the east–west direction, but with currents from the east more prevalent. The sediment temperature in the river mouth and in the south channel was similar at 8–9°C. It was only 6°C in the east channel. These results suggested that the river water flows predominantly through the south channel. The temperature difference or flow difference may explain the apparent increase in carbonates in the south channel relative to the east channel. The average of nine samples (#37–45) from the south channel, compared to five samples (#17–21) in the east channel, had values for Ca, Mg, and inorganic carbon greater by 1.5, 0.8, and 0.5% (136, 116, 171% increase), respectively. Also, the core at station 20 had lower Ca values throughout its entire 50 cm length, suggesting that this deficiency has been long term. X-ray diffractograms from the less than 2 μm fraction of samples 13 and 38 showed a similar mineralogical composition, but a repeat analysis of a bulk sample (total size range of sample 13) yielded a strong dolomite peak. This suggests a possible correlation between silt-size particles and carbonates as has been previously observed in other Great Lakes (Thomas et al. 1972, 1973). Erosion of glacial sediments provides the most likely source of silt-size dolomite for this enrichment in carbonates. Zoltai (1965) reported occurrences of glaciolacustrine deposits of varved clays in the

TABLE 2. Summary table giving means and standard deviations of individual variables in five zones of the study area.

	River mouth 6 Samples		Near mill 11 Samples		NE. fringe 6 Samples		East channel 9 Samples		South channel 11 Samples	
Variables	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD
% SiO_2	62.9	0.36	58.2	3.3	61.8	0.28	61.6	0.74	60.6	0.48
% Al_2O_3	9.0	0.36	8.7	0.57	10.0	0.28	10.3	0.31	9.9	0.34
% MgO	5.2	0.19	5.2	0.59	5.5	0.10	5.3	0.33	5.9	0.21
% CaO	7.0	0.63	6.1	0.47	5.4	0.28	4.7	0.63	5.9	0.57
% Na_2O	2.8	0.07	2.5	0.28	2.9	0.11	2.8	0.08	2.9	0.09
% K_2O	2.1	0.11	2.0	0.15	2.4	0.05	2.5	0.10	2.3	0.11
% TiO_2	0.55	0.02	0.60	0.04	0.64	0.03	0.68	0.03	0.64	0.02
% P_2O_5	0.21	0.001	0.22	0.03	0.20	0.01	0.19	0.01	0.27	0.02
% MnO	0.11	0.02	0.08	0.001	0.13	0.02	0.15	0.02	0.12	0.02
% S	0.03	0.001	0.07	0.04	0.03	0.01	0.03	0.01	0.01	0.01
% Fe_2O_3	4.4	0.25	4.6	0.22	5.4	0.16	5.7	0.24	5.5	0.17
Cr μg/g	39.4	25.1	45.8	17.5	38.7	5.6	86.2	24.5	61.0	14.6
Cu μg/g	30.6	2.1	36.6	6.3	37.4	1.4	37.9	2.9	36.9	2.0
Ni μg/g	31.3	6.8	32.4	9.4	37.0	3.2	56.4	8.9	52.4	4.3
Pb μg/g	26.9	2.8	23.5	4.9	34.2	2.1	35.2	3.8	31.5	3.5
% Org. C	1.87	0.08	5.41	3.4	1.82	0.46	1.40	0.26	1.48	0.32
% Inorg. C	1.47	0.18	1.33	0.14	1.18	0.14	0.89	0.23	1.35	0.21
Hg μg/g	0.05	0.02	0.18	0.10	0.13	0.04	0.11	0.05	0.10	0.04
% Silt	63.6	8.2	66.2	10.1	41.9	3.7	45.9	4.8	42.8	7.4
% Clay	35.6	8.7	32.4	11.9	57.9	3.6	53.8	5.2	57.0	7.4
Depth m	11.0	4.1	15.1	6.4	9.3	2.5	11.7	2.9	17.4	8.2
Temp. °C	8.5	0.43	8.1	0.96	7.0	0.26	6.3	0.71	8.6	0.74
Eh mv	87.3	6.9	113.	33.6	89.5	14.8	106.	70.7	106.	37.7
pH	6.9	0.24	6.3	0.42	6.7	0.24	6.9	0.26	6.8	0.26

Lake Nipigon basin which contained 16–26% carbonates by weight. In addition, the ground morainic till generally reflects the composition of the bedrock and in this area may contain up to 15% calcium carbonite in the fine matrix. Also, the glacial sediment in core 35 showed a 2–3% increase in Ca over the recent muds above it.

The usual relationship between organic carbon, clay-size fraction, and trace elements (Thomas 1972, 1973; Thomas et al. 1972, 1973) did not exist in these samples. This is presumably due to the influence of organic fibers. There was a strong relationship between organic carbon, total-S, and Hg. Most of the S is presumably organic-S and not sulphides, as indicated by the poor Fe to S relationship. Two of the adsorption processes by which Hg may be found in a sediment may explain the association of Hg with organic carbon and S (Jonnasson 1970). They are: (1) irreversible adsorption of mercury by sulphide surfaces, and (2) covalently-bonded sulfo-organometallic compounds. It should also be noted that, while the mill effluent is exceedingly alkaline, the sediment samples around the outfall are quite acidic ($pH < 6.0$). These observations would suggest that organic matter from the outfall is being decomposed on the bottom with the production of organic acids which have the effects of lowering the pH level.

The strong Al to Fe correlation agrees with results of Williams et al. (1971) and of Vernet and Thomas (1972), who suggest that Fe is predominantly in the form of hydrated Fe oxides which occur as coatings on individual clay particles. The Si to Na correlation suggests the presence of quartz and alkali feldspar (Thomas 1969).

Major element concentrations reflect the presence of illite, quartz and feldspar within the area. Carbonates appear to show a preferred relationship with the silt-size fraction and with the south channel and are derived from the Nipigon River.

The results show that the two primary effects of mill discharge on the sediments are a decrease in pH and an increase in organic matter within 1.5 km of the point source. Above average concentrations of total-S and Hg appear to be associated with this organic matter. Total-S (Fig. 2) and organic carbon (Fig. 3) concentrations delineate the zone of significant effects of the mill effluent. Anomalies beyond this area do not depart markedly from background values.

Acknowledgments

I am most indebted to the many colleagues at C.C.I.W. who provided guidance and criticism in preparing this contribution. I would also like to thank R. J. Stedwill and J. VanderWal from the Ontario Ministry of Environment for their assistance in sampling and the Water Quality Lab at C.C.I.W. for the mercury analyses. P. G. Sly, Chief, Process Research Division, is acknowledged for permission to publish.

Allersma, E., and A. J. de Groot. 1974. Field observations on the transport of heavy metals in sediment. Delft Hydraul. Lab. Publ. No. 122.

Beak, T. W., Consultants Ltd. 1969. Waste treatment study. Proj. M 47–7–7E. 95 p.

Callender, E. 1969. Geochemical characteristics of Lakes Michigan and Superior sediments. Proc. Conf. Great Lakes Res. 12: 124–160.

Cameron, E. M. 1967. A computer program for factor analysis of geochemical and other data. Geol. Surv. Can. Pap. 67–34.

Davis, J. C. 1973. Statistics and data analysis in geology. John Wiley and Sons, Inc., New York, N.Y. 550 p.

Duncan, G. A., and N. A. Rukavina. 1972. The Sedigraph grain-size analyser — an alternative to pipette analysis. Proc. Conf. Great Lakes Res. 15: (Abstracts)

Freund, J. E. 1970. Statistics, a first course. Prentice-Hall, Inc., Englewood Cliffs, N.J. 340 p.

Jonasson, I. R. 1970. Mercury in the natural environment: a review of recent work. Geol. Surv. Can. Pap. 70–57.

Kemp, A. L. W., C. B. J. Gray, and A. Mudrochova. 1972. Changes in C, N, P and S in the last 140 years in three cores from Lakes Ontario, Erie and Huron, p. 251–279. *In* H. E. Allen and J. R. Kramer [ed.] Nutrients in natural waters. John Wiley and Sons, Inc., New York, N.Y.

Mothersill, J. S., and P. C. Fung. 1972. The stratigraphy, mineralogy and trace element concentrations of the Quaternary sediments in the Northern Lake Superior Basin. Can. J. Earth Sci. 9: 1735–1755.

Nussman, D. G. 1965. Trace elements in the sediments of Lake Superior, Ph.D. Thesis. Univ. Michigan, Ann Arbor, Mich. p. 243.

Polak, J., and M. D. Palmer. 1977. Plume dynamics and chemistry. J. Fish. Res. Board Can. 34: (This issue)

Pye, E. G. 1962. Geology and scenery along the north shoreline of Lake Superior. Ont. Dept. Mines, Geol. Circ. 10: 81 p.

Rukavina, N. A., and R. K. Dolling. 1973. Sizdist: statistical analysis for F.A.S.T. grain-size data. Proc. Conf. Great Lakes Res. 16.

Sandilands, R. G. 1975. Can. Cent. Inland Waters Intern. Rep.

Shimp, N. F., et al. 1971. Trace element and organic carbon accumulation in the most recent sediments of southern Lake Michigan. Ill. State Geol. Surv., Environ. Geol. Notes 41: 25 p.

Sly, P. G. 1969. Bottom sediment sampling. Proc. Conf. Great Lakes Res. 12: 883–898.

Sly, P. G., and R. L. Thomas. 1974. Review of geological research as it relates to an understanding of Great Lakes limnology. J. Fish. Res. Board Can. 31: 795–825.

Thomas, R. L. 1969. A note on the relationship of grain size, clay content, quartz and organic carbon in some Lake Erie and Lake Ontario sediments. J. Sediment. Petrol. 39: 808–809.

1972. The distribution of mercury in the sediments of Lake Ontario. Can. J. Earth Sci. 9: 636–651.

1973. The distribution of mercury in the surficial sediments of Lake Huron. Can. J. Earth Sci. 10: 194–204.

Thomas, R. L., A. L. W. Kemp, and C. F. M. Lewis. 1972. Distribution, composition and characteristics of surficial sediments of Lake Ontario. J. Sediment. Petrol. 42: 66–84.

1973. The surficial sediments of Lake Huron. Can. J. Earth Sci. 10: 226–271.

Vernet, J. P., and R. L. Thomas. 1972. The occurrence and distribution of mercury in the sediments of the Petit Lac (Western Lake Geneva). Eclogae Geol. Helv. 65/2: 307–316.

Water Survey of Canada. 1972. Surface Water Data, Ontario.

Williams, J. D. H., J. K. Syers, S. S. Shukla, and R. L. Harris. 1971. Levels of inorganic and total phosphorous in lake sediment as related to other sediment parameters. Environ. Sci. Technol. 5: 113–1120.

Zoltai, S. C. 1965. Glacial features in the Quetico–Nipigon area, Ontario. Can. J. Earth Sci. 2: 247–269.

Relation between Nipigon Bay Benthic Macroinvertebrates and Selected Aspects of Their Habitat[1]

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VANDER WAL, J. 1977. Relations between Nipigon Bay benthic macroinvertebrates and selected aspects of their habitat. J. Fish. Res. Board Can. 34: 824–829.

In areas of Nipigon Bay unaffected by pulp and paper mill effluent, the benthic macroinvertebrate community was characterized by low standing stocks and high diversity. The coefficient of community and percentage similarity of community defined two major environments in Nipigon Bay, generally related to distance from the mill outfall. Near the pulp and paper mill outfall, further zonation of the benthic macroinvertebrate community was apparent. Inhibition and ultimate extinction of oligochaete populations appeared related to increasing levels of organic carbon and total sulphur, both associated with proximity to the outfall. Since a 10-yr period following abatement measures has not resulted in major responses by the macroinvertebrate community, recovery is expected to be slow.

VANDER WAL, J. 1977. Relation between Nipigon Bay benthic macroinvertebrates and selected aspects of their habitat. J. Fish. Res. Board Can. 34: 824–829.

Dans les régions de la baie Nipigon qui ne sont pas affectées par l'effluent de moulins de pâte et de papier, la communauté de macroinvertébrés benthiques est caractérisée par une faible biomasse et une forte diversité. Le coefficient de communauté et la similitude de communauté en pourcentage servent à définir deux environnements majeurs dans la baie Nipigon, liés en général à la distance de l'émissaire du moulin. Près de l'émissaire du moulin de pâte et de papier, d'autres zones sont évidentes dans la communauté de macroinvertébrés benthiques. L'inhibition et finalement l'extinction des populations d'oligochètes semblent liées aux niveaux croissants de carbone organique et de soufre total, tous deux associés à la proximité de l'émissaire. Etant donné qu'une période de 10 ans s'est écoulée depuis l'application de mesures de suppression sans provoquer de réponses majeures de la part de la communauté de macroinvertébrés, on s'attend que le rétablissement sera lent.

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THE general level of production, or trophic status, may be expected to influence the distribution and abundance of many benthic macroinvertebrates (Johnson and Brinkhurst 1971). Furthermore, the very processes of production may couple with perturbative factors to directly alter the benthic environment. Consequently, I sought to determine the number and character of the benthic macroinvertebrate communities in Nipigon Bay and, where possible, relate these parameters to habitat conditions associated with the pulp and paper mill operating there.

Aspects of the Lake Superior benthic macroinvertebrate community have been presented by Henson (1966), Hiltunen (1969), and more recently Cook and Johnson (1974). Studies in Nipigon Bay itself have, however, been limited (Thomas 1966; Freitag et al. 1973). The attempts made to relate structure of benthic macroinvertebrate communities to the influence of the pulp and paper mill (German 1968; Beak 1970; Brouzes 1971) have differed widely in their interpretations as to the severity and extent of the mill effects. This study sought to further interpretive capabilities for the association of benthos to specific substrate characteristics described by Sandilands (1977).

Methods

COLLECTION AND IDENTIFICATION OF MACROINVERTEBRATES

Sampling was carried out on a longitudinal and latitudinal grid at 30-s intervals. Eleven stations (Fig. 1), not confined to the grid system, were sam-

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

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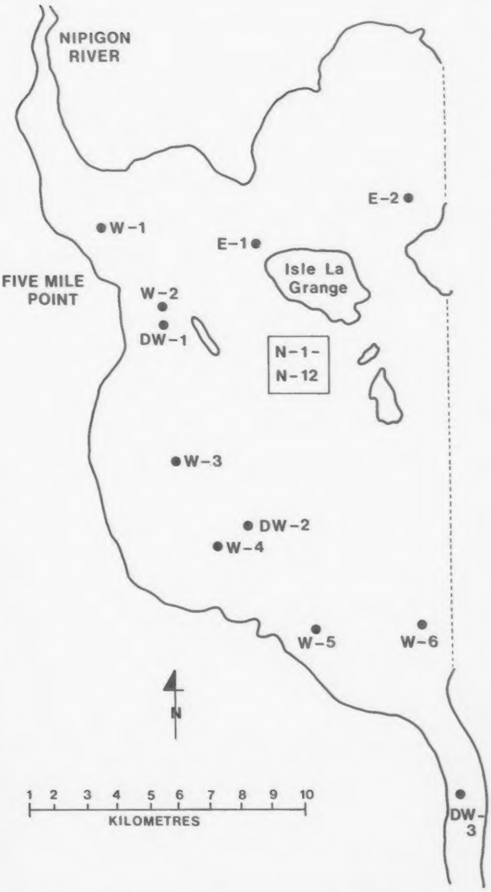

FIG. 1. Nipigon Bay macroinvertebrate study area.

pled 15 times with the exception of one which was sampled only 10 times. Replicate samples at 20 m were taken at eight stations in the eastern and southern channels and remaining stations were sampled at 50 m. A further 11 stations were established at varying depths between the effluent outfall and Five Mile Point. Stations were located by dead reckoning from marker buoys and prominent landmarks and by comparison of depths recorded by an echo sounder (Furuno F-200) to those on Canadian Hydrographic Chart 2312.

Each Ponar grab sample was 500 cm^2. Macroinvertebrates and coarse debris were separated from the finer substrate by an 8 mesh cm^{-1} boxed screen. Gross substrate characteristics were noted on collection. Later, coarse screened samples were concentrated further and preserved in ethanol.

General invertebrate taxonomy was according to Pennak (1953) while additional consultations from appropriate keys were employed when required.

COMMUNITY COMPARISONS

Two measures were used to identify associations of macroinvertebrates, the "coefficient of community" (CC), and "percentage similarity of community" (PSc) (Whittaker and Fairbanks 1958; Johnson and Brinkhurst 1971). The coefficient of community measures the percentage of taxa shared by two samples as:

$$CC = \frac{c}{a + b - c} \cdot 100$$

where a is the number of taxa in the first sample, b is the number of taxa in the second, and c is the number of taxa common to both. The coefficient of community emphasizes likeness of samples on the basis of similar distributions of constituent taxa without regard to aspects involving relative abundance. Relative abundance is, however, included in the percentage similarity of community

$$PSc = 100 - 0.5\,\Sigma\,|a' - b'| = \Sigma \min\,(a', b')$$

in which a' and b' are, for each taxon, the respective percentages of total animals in samples A and B. Both indices have values between 0 and 100, representing the lowest and highest affinity, respectively, between two samples.

Each measurement has its advantages and limitations (Whittaker and Fairbanks 1958). The coefficient of community overvalues rarer species which the percentage similarity of community largely neglects. Used together, the two indices are useful not only in describing the nature of affinities between samples but also in distinguishing between environmental factors influencing macroinvertebrate distributions.

Both indices were computed for all comparisons among the 11 stations at which replicate samples were collected. The 15 samples from one station, W-3, were subdivided into 5 sets of 3 and the CC and PSc were computed, providing criteria for establishing levels of affinity. Station W-3 with the greatest diversity of taxa was selected since it would be expected to produce minimum values for CC and PSc in establishing limits for high affinity between samples. Values for CC ranged from 42 to 89 with a mean of 68 while PSc values ranged from 69 to 85 with a mean of 77. The minimum values, CC = 42 and PSc = 64, were considered the lowest limits which indicated high affinity. Values of one half of these, that is a CC of 21 and a PSc of 32, were arbitrarily taken as separating sets with low and intermediate affinity.

SURFICIAL SEDIMENT CHARACTERISTICS

Sandilands (1977) revealed, through cluster analysis of a coefficient of correlation matrix, the existence of five zones or environments as follows:

1) Nipigon River mouth area, characterized by the highest values for calcium and inorganic carbon,

2) Eastern channel area, characterized by high values for a cluster of variables associated with clay minerals,

3) Mill outfall area distinguished by the highest

TABLE 1. Mean macroinvertebrate densities (500 cm^{-2}) from 11 areas of Nipigon Bay.

Station depth (*m*)	W-1 20	W-2 20	W-3 20	W-4 20	W-5 20	W-6 20	E-2 20	E-2 20	DW-1 50	DW-2 50	DW-3 50
Ephemera stimulans	—	—	0.20	—	0.07	—	0.07	0.07	—	0.07	—
Hexagenia limbata	0.07	—	0.20	0.27	0.13	0.07	0.13	—	—	—	—
Limnephilidae	—	—	—	—	—	—	—	—	—	0.07	—
Chironomidae	6.13	4.93	1.80	1.47	2.33	4.30	2.27	1.60	3.47	3.67	7.90
Palpomyia spp.	—	—	0.07	—	—	—	—	—	—	—	—
Asellus spp.	—	—	0.20	—	—	—	—	—	—	0.13	—
Pontoporeia affinis	0.40	—	6.93	10.0	29.00	33.87	20.33	50.13	—	0.07	8.40
Mysis relicta	—	—	—	—	—	—	—	—	0.07	0.47	—
Pisidium spp.	2.13	0.20	1.13	1.87	1.00	0.73	3.33	1.80	—	1.80	1.10
Sphaerium spp.	0.33	—	1.53	0.07	—	—	—	—	—	—	—
Unionidae	0.07	—	—	—	—	—	—	—	—	—	—
Valvata sincera	0.13	—	0.87	0.53	0.67	—	1.33	—	—	0.40	—
V. tricarinata	—	—	—	0.13	0.07	—	—	—	—	—	—
Oligochaeta	6.53	66.27	5.07	7.47	0.13	0.87	20.00	7.73	404.67	71.27	10.90
Acari	0.13	—	0.20	—	—	0.47	0.07	—	—	—	—

values for organic carbon, total sulphur, mercury and reduced pH, where organic carbon and total sulphur were strongly correlated ($r = .921$),

4) Northeast fringe area comprising a transitional zone between 1, 2, and 3 above,

5) South channel zone yielding high values for magnesium and phosphrus.

The three major sedimentary zones (east channel, south channel, and mill area) were utilized in comparisons with apparent zones delimited on the basis of macroinvertebrate distributions. All following reference to chemical characteristics of Nipigon Bay sediments is from Sandilands (1977).

Results

MACROINVERTEBRATE DISTRIBUTION

The relative densities and diversity of macroinvertebrates (Table 1) indicated that although most taxa were commonly widespread, organismic abundance was greatly influenced in certain areas associated with the mill outfall.

Analysis of the 11 sets of data from the replicate sampling (Fig. 2) yielded the following observations. High affinity for the CC was noted in 26 of the 55 comparisons. Little if any affinity was found in only 5 of the comparisons and all of these involved station DW-1 where only three taxa were collected. Twenty-two of the 29 comparisons indicating low or intermediate affinity

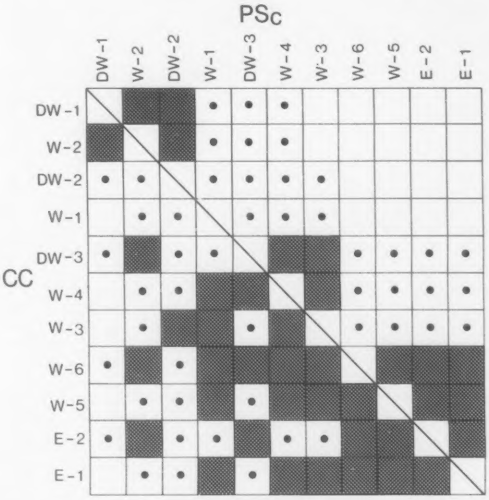

FIG. 2. Values of the coefficient of community (CC, lower triangle) and percentage similarity of community (PSc, upper triangle) for 11 stations, replicate sampled in Nipigon Bay. Solid squares indicate high affinity between macroinvertebrates of two stations; dots, intermediate affinity; open squares; little if any affinity.

TABLE 2. Macroinvertebrate densities (m^{-2}) and frequency (%) of occurrence from two areas associated with the mill outfall.

	Mill area A[a]		Mill area B-1[b]	
Macroinvertebrates	Density 500 cm^{-2}	Frequency (%)	Density 500 cm^2	Frequency (%)
Palpomyia spp.	—	—	0.40	6.7
Tendipedidae	0.28	14.2	6.70	87.0
Pisidium spp.	—	—	0.10	6.7
Amnicola spp.	0.14	14.3	0.20	6.7
Valvata sincera	—	—	0.10	6.7
Hyallela azteca	—	—	0.90	13.3
Oligochaeta	0.14	14.3	106.0	73.3

[a] pH, 5.5; % Organic C, 21.7; % Total S, 0.26.
[b] pH, 6.3; % Organic C, 4.6; % Total S, 0.06.

were associated with stations DW-1, W-2, and DW-2. With the exception of these three stations, relatively high affinity was widespread.

High affinity for PSc was found in only 12 of the comparisons while 25 comparisons indicated intermediate affinity. Three distinct associations were noted in the PSc analyses. Firstly, stations DW-1, W-2, and DW-2 vere very similar in composition, as the PSc in this group had values of 94, 95, and 96. A second group with high affinity involved stations DW-3, W-3, and W-4. The third and largest group of stations showing high similarity was composed of W-5, W-6, E-1, and E-2. The second distinct group was associated with the first and third in a manner indicating intermediate affinity while little if any affinity between the first and third groups was noted.

A comparison of the three macroinvertebrate associations, or groups, with the three major sediment zones indicated that since both the CC and PSc comparisons between eastern and southern channel stations showed a high degree of affinity, only two major environments are evidenced: that area associated with the mill outfall and that area not associated with the mill outfall.

DISTRIBUTION OF SEDIMENTS AND MACROINVERTEBRATES IN THE MILL AREA

Although the mill area was described as a single major zone on the basis of sediment characteristics (Sandilands 1977), two distinctly different areas are present (R. G. Sandilands personal communication). The near-outfall area "A" was characterized by extremely high organic carbon, total sulphur, and mercury levels and consequently two stations in this area were omitted by Sandilands (1977) from the cluster analysis for statistical reasons. Analysis of the distribution of benthic fauna in the mill area

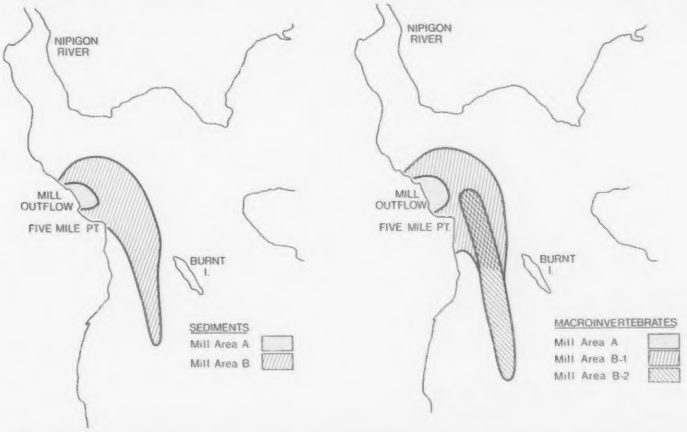

FIG. 3. Major sediment and macroinvertebrate zones found in Nipigon Bay.

indicated three distinctly different zones (Fig. 3). The first was coincident with the near outfall area "A" while the second, "B-1," and third, "B-2," were found in the intermediate outfall area, consequently subdividing the sediment zone "B."

Seven stations sampled in mill area "A" revealed the virtual absence of macroinvertebrates (Table 2), while 15 stations sampled in mill area "B-1" indicated an overall depression of taxon diversity with high oligochaete numbers in the deeper waters. The third macroinvertebrate zone, mill area "B-2," included stations W-2, DW-1, and DW-2 where the mean oligochaete density for 45 samples was 3600 m^{-2}.

Inhibition and ultimate extinction of oligochaete populations appears related to increasing levels of organic carbon and total sulphur (Fig. 4). Organic carbon levels of greater than 3.4% and total sulphur levels of greater than .049% were accompanied by a reduction of oligochaete numbers.

Spatial Distribution of Macroinvertebrates in the South Channel

The distribution of "tolerant" oligochaete and "intolerant" *Pontoporeia affinis* (Fig. 5 and 6) shows progressively greater stress towards the mill. Furthermore, sampling at the 20 and 50 m depths indicate that deeper water areas were subject to greater stress than shallow areas. Stations W-2 and DW-1 had both a low organismic diversity and high oligochaete numbers. The oligochaetes comprised a tubificid association in which *Tubifex tubifex* and *Limnodrilus hoffmeisteri* were well represented. The absence of *P. affinis* in the deeper waters further emphasized a vertical stress gradient in the southern channel.

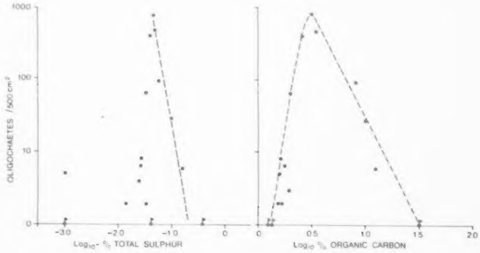

FIG. 4. The relationships between oligochaete numbers and organic carbon, and oligochaete numbers and total sulphur, derived from 16 stations at which benthic fauna sampling and sediment sampling were coincident. Flags denote 0 values.

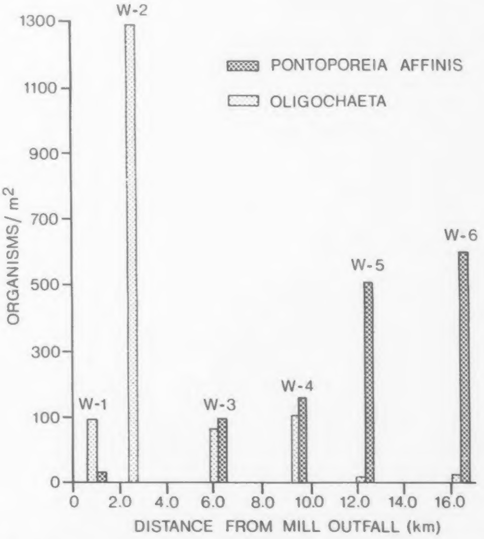

FIG. 5. Numbers of oligochaeta and *Pontoporeia affinis* in relation to distance from the mill outfall at 20.0 m.

Discussion

The relationship between total sulphur and oligochaete numbers is likely a fortuitous one unless substrate concentrations of sulphur are directly related to production of H_2S or other compounds known to be toxic (Van Horn et al. 1949; Smith and Oseid 1972) in the interstitial sediments and sediment–water interface. The significance of this relationship is that since increasing levels of organic carbon are not expected to cause conditions which will inhibit pollution tolerant oligochaetes, some factor or group of factors related to the deposition of organic materials originating from the mill must be present in toxic proportions.

An investigation of some toxic organic compounds in the Nipigon Bay sediments (Fox 1976) has indicated that dehydroabietic acid is distributed in a similar, though somewhat more extensive manner than organic carbon. Unfortunately, investigations of any toxic materials associated with organics in the sediments will not readily provide an explanation for reduced or eliminated tolerant macroinvertebrates without precise information about the relationship between such substrate contaminants and levels in the microhabitats associated with the sediment–water interface. In the absence of this information, organic carbon appears to provide an appropriate index of "stress" in the benthic environment.

The increase in numbers of *P. affinis* with in-

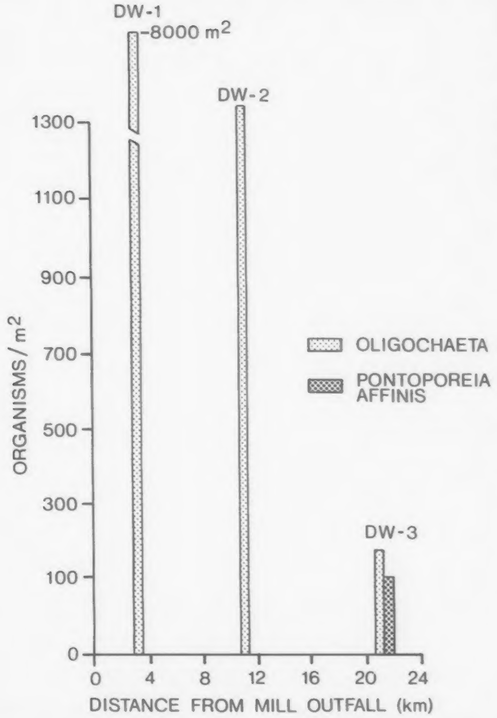

FIG. 6. Numbers of oligochaeta and *Pontoporeia affinis* in relation to distance from the mill outfall at 50.0 m.

creasing distance from the mill is probably at least partly due to the transitional nature of the area from a lotic to lentic environment. Although *P. affinis* has been found to be the dominant species in Lake Superior and associated bays (Adams and Kregear 1969; Hiltunen 1969; Freitag et al. 1973), its distribution in the Nipigon River and Helen Lake north of Nipigon Bay was limited (Ontario Ministry of the Environment, unpublished data). This transitional trend, however, does not acocunt for the total absence of *P. affinis* in the deeper waters of the southern channel from the mill to a point at least 10.5 km downstream.

Industrial pollution abatement measures usually take the form of on-site modifications to processes and treatment systems. Consequently, improvements in the benthic environment may not necessarily be expected in the short term since they depend on the natural ability of the receiving waters to flush and degrade accumulated contaminants.

Among the abatement measures effected at the Red Rock mill since 1969 was the provision for primary clarification of the effluent in 1972. Comparisons with macroinvertebrate data from earlier studies (German 1968; Beak 1970; Brouzes 1971) in fact indicate that there have been few if any significant alterations in the benthic community in the associated period. Clearly, since the earlier descriptions of pulp fiber deposits indicate that there has been little change up to the present, major alterations in macroinvertebrate communities are not expected for some time.

Acknowledgments

Thanks are extended to D. J. Hollinger and J. D. Fitzsimons for their participation in the field collections. Drs M. G. Johnson, C. K. Minns, and J. R. M. Kelso were instrumental in the preparation of this paper.

ADAMS, C. E., AND R. D. KREGEAR. 1969. Sedimentary and faunal environments of eastern Lake Superior. Proc. Conf. Great Lakes Res. 12: 1–20.

BEAK, T. W., CONSULTANTS LTD. 1970. Biological survey of Nipigon Bay. Proj. T-3092.

BROUZES, R. J. P. 1971. Red Rock effluent studies, biological survey. Domtar Res. Cent. Proj. 71-4111-03: 1–33.

COOK, D. G., AND M. G. JOHNSON. 1974. Benthic macroinvertebrates of the St. Lawrence Great Lakes. J. Fish. Res. Board Can. 31: 763–782.

FOX, M. E. 1977. Persistence of dissolved organic compounds in kraft pulp and paper mill effluent plumes. J. Fish. Res. Board Can. 34. (This issue)

FREITAG, R., P. FUNG, J. S. MOTHERSILL, AND G. K. PROUTY. 1973. Geographical distribution and spatial relationships of benthic macroinvertebrates of Nipigon Bay, Lake Superior, Ontario. Lakehead Univ. MS Rep: 1–29.

GERMAN, M. J. W. 1968. Biological survey of Nipigon Bay 1966–1967. Ont. Water Resour. Comm. Rep. p. 1–22.

HENSON, E. B. 1966. A review of Great Lakes benthos research. Great Lakes Res. Div., Univ. Mich. Publ. 14: 37–54.

HILTUNEN, J. K. 1969. Invertebrate macrobenthos of Western Lake Superior. Mich. Acad. Sci. 1: 123–133.

JOHNSON, M. G., AND R. O. BRINKHURST. 1971. Associations and species diversity in benthic macroinvertebrates of Bay of Quinte and Lake Ontario. J. Fish. Res. Board Can. 28: 1683–1697.

PENNAK, R. W. 1953. Freshwater invertebrates of the United States. The Ronald Press Company, New York, N.Y.

SANDILANDS, R. G. 1977. Effect of pulp mill effluent on the surficial sediments of western Nipigon Bay, Lake Superior. J. Fish. Res. Board Can. 34. (This issue)

SMITH, L. L., AND D. M. OSEID. 1972. Effects of hydrogen sulphide on fish eggs and fry. Water Res. 6: 711–720.

THOMAS, M. L. H. 1966. Benthos of four Lake Superior Bays. Can. Field Nat. 80: 200–212.

VAN HORN, WM., J. B. ANDERSON, AND M. KATZ. 1949. The effect of Kraft pulp wastes on some aquatic organisms. Trans. Am. Fish. Soc. 79: 55–63.

WHITTAKER, R. H., AND C. W. FAIRBANKS. 1958. A study of plankton and copepod communities in the Columbia Basin, southeastern Washington. Ecology 39: 46–65.

Distribution of Some Organic Compounds in the Receiving Waters of a Kraft Pulp and Paper Mill[1]

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BROWNLEE, B., AND W. M. J. STRACHAN. 1977. Distribution of some organic compounds in the receiving waters of a kraft pulp and paper mill. J. Fish. Res. Board Can. 34: 830–837.

Water, seston, sediment, and macrophyte samples were collected from Nipigon Bay, Lake Superior at distances up to 6.8 km from the effluent discharge of a kraft pulp and paper mill at Red Rock, Ontario. Fifteen compounds have been identified in mill effluent and six of these were found in samples from the Bay. Mill-related compounds were found most often in water and sediment samples, less often in seston samples, and in none of the macrophytes samples. Dehydroabietic acid, present in mill effluent in excess of 1 mg/ℓ, was found in most water and sediment samples and a few seston samples. This compound is a good indicator of the areal influence of the effluent. Palmitic acid and dioctyl phthalate were also widely distributed. Acetovanillone and sandaracopimaric acid were found in one water sample 1.0 km from the discharge. 7-oxodehydroabietic acid was found in five water samples at distances of up to 4.7 km from the discharge. This is apparently the first time that this compound has been reported in a mill effluent or in environmental samples.

BROWNLEE, B., AND W. M. J. STRACHAN. 1977. Distribution of some organic compounds in the receiving waters of a kraft pulp and paper mill. J. Fish. Res. Board Can. 34: 830–837.

Nous avons prélevé des échantillons d'eau, de seston, de sédiments et de macrophytes dans la baie Nipigon, lac Supérieur, à des distances allant jusqu'à 6.8 km de l'émissaire d'un moulin de pâte et de papier kraft à Red Rock, Ontario. Quinze composés ont été identifiées dans l'effluent du moulin, dont six ont été retrouvés dans les échantillons de la baie. Les composés associés au moulin se rencontrent le plus souvent dans les échantillons d'eau et de sédiments, moins souvent dans les échantillons de seston et jamais dans les échantillons de macrophytes. L'acide déshydroabiétique, présent dans l'effluent du moulin à des concentrations dépassant 1 mg/ℓ, se trouve dans la plupart des échantillons d'eau et de sédiments, et dans quelques échantillons de seston. Ce composé est un bon indicateur de l'étendue de l'influence de l'effluent. L'acide palmitique et le phthalate de dioctyl sont aussi largement répandus. On a trouvé de l'acétovanillone et de l'acide sandaracopimarique dans un échantillon d'eau prélevé à 1 km de l'émissaire. On a trouvé de l'acide 7-oxodéshydroabiétique dans cinq échantillons d'eau à des distances allant jusqu'à 4.7 km de l'émissaire. C'est la première fois, sembe-t-il, que ce composé est signalé dans un effluent de moulin ou dans des échantillons de l'environnement.

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PULP and paper mills are major contributors of waste materials to receiving waters in Canada (Marier 1973). This waste discharge may cause problems such as high biochemical oxygen demand, undesirable aesthetic effects, fish tainting, or toxicity to fish and other aquatic life. Dissolved organic compounds can account for much of the acute toxicity of pulp and paper mill effluents (Rogers 1973; Rogers et al. 1975; Leach and Thakore 1973, 1975) and may be an important cause of fish tainting (Shumway and Palensky 1973; Thomas 1973). Most studies to date have been on whole effluent or individual effluent streams. Only a few studies (Keith and Hercules 1973; Maenpaa et al. 1968) have been concerned about the survival of specific compounds in receiving waters adjacent to mills. The purpose of the present study was to investigate the distribution and fate of organic compounds from a pulp and paper mill effluent in the adjacent receiving waters. Identification of organic compounds in the mill effluent was a prerequisite for the investigation.

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

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Red Rock, Ont., at the western end of Nipigon Bay was the site for field studies in the summer of 1974. The bay receives effluent, discharged as a point source, from a kraft pulp and paper mill which is the major industry in the area. For a kraft pulp mill using softwood, some types of compounds to be expected in the effluent are phenols, fatty acids, resin acids, and modified derivatives of these, e.g. chlorinated materials produced during chlorine bleaching (Das et al. 1969; Rogers 1973; Rogers and Keith 1974; Leach and Thakore 1975). The total effluent at this mill was made up of three major streams — the "clarifier" which contained the effluent from the digestion and washing processes and was subjected to primary treatment; the "low suspended solids" which was untreated and includes the evaporator and bleaching wastes; and the "uncontaminated" stream which comprised the miscellaneous plant wastes and those of the town of Red Rock.

The distribution of materials from the effluent in the receiving waters will depend on loading, dilution, and water movement, partitioning between trophic levels or compartments, and removal processes such as biodegradation and sedimentation. It was anticipated that more persistent materials would be detectable at significant distances (several kilometres) from the effluent discharge, and that their distribution would depend more on overall water movement than on day-to-day movement of the surface effluent plume. For this reason, the study concentrated on the region beyond the visual plume and covered an area of approximately 25 km^2. Water, seston (particulate), sediment, and macrophyte samples were collected and investigated for identifiable organic compounds which could be related to the mill effluent. Concurrent chemical studies focused on the dynamics of dissolved organic compounds within the effluent plume (Fox 1977), organic compounds in fish (Kaiser 1977), and the distribution of a specific compound, dehydroabietic acid, in the sediments adjacent to the mill (Brownlee et al. 1977). These studies, in turn, were part of a multidisciplinary investigation on the impact of pulp and paper mill waste discharged into Lake Superior.

Materials and Methods

SAMPLE COLLECTION AND PROCESSING

Each of the 15 stations in Fig. 1 was sampled at least once for water and seston over a 3-wk period (July 15–August 3, 1974). Water samples of about 35 ℓ were collected from a depth of 5 m (less in shallow water) by aspiration through teflon tubing into a stainless steel pressure tank. The sample was pressure filtered through a cleaned Sartorius teflon and stainless steel apparatus using 10 psi or less of nitrogen, purified by passing through molecular sieves. The 142-mm Nucleopore glass fiber filters used were precombusted at 450 C for 8 h and had a nominal pore size of 0.8 μm; two such filters were required per sample. The glass fiber filters were frozen. Four sediment samples (stations 2, 8, 14, and 19) were collected by Shipek sampler and also frozen until extracted. Macrophyte samples collected from sites designated "M" close to shore in shallow water, were rinsed with "organic free" water and stored frozen.

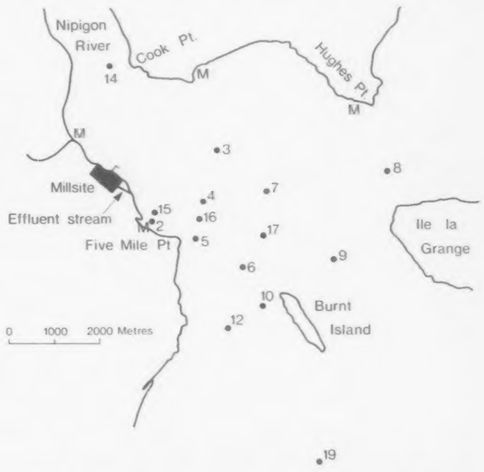

FIG. 1. Location of sample stations with corresponding station numbers including macrophytes (M).

A 9-ℓ portion of the filtrate was subjected to extraction on the sampling date. All organic solvents used were distilled in glass and were residue-free. The water samples were made saline (0.1 N) with precombusted sodium chloride and continuously extracted with 700 ml of chloroform for 22 h. The extracts were taken to dryness at 60°C, the amount of extracted material was determined, and the residue was methylated with diazomethane in diethyl ether–methanol. The seston filters were thawed and homogenized with 150 ml of chloroform–methanol (2:1, vol/vol). After heating under reflux for 1 h, the mixture was filtered, and two drops of 6N hydrochloric acid were added to the filtrate which was then taken to dryness and methylated. Sediment samples were freeze-dried and extracted with chloroform for 24 h in an all-glass Soxhlet apparatus. Extracts were subjected to the same procedures as those employed with the water samples. Freeze-dried macrophyte samples were treated in the same manner as the sediment samples except that benzene was used as the extracting solvent.

QUALITATIVE ANALYSIS

The methylated extracts were taken up in a small volume of benzene, and analyzed by gas chromatography (GC) using a flame ionization detector (FID). GC conditions were: 1.8 m × 3 mm stainless steel column, 3% OV-1 on Chromsorb W-HP, 125–250°C at 6°C/min, nitrogen carrier, 20 ml/min. An aliquot was also examined by gas chromatography–mass spectrometry (GC–MS) using the same chromatographic conditions except that a glass column was used and helium was the carrier gas. The gas chromatograph was coupled via a glass jet separator to a computer-operated Finnigan model 1015 S/L quadropole mass spectrometer. The electron impact mass spectral data thus obtained were used to identify components in the extracts by conducting Biemann-type spectrum searches (Heller 1972; Hertz et al. 1971; Hoyland and Neher 1974) of a computer-based library of mass spectra. The similarity index generated in this type of spectrum search is a measure of the confidence that can be placed in the identification; a perfect match would give a similarity index of 1.00. Known compounds gave similarity indices greater than 0.4. Differentiation between compounds in a methylene homologous series required higher similarity indices (approximately 0.7) and the use of GC retention times as additional information. The presence or absence in other extracts of a compound thus identified was established on the basis of its appearance in the total ion chromatograms and characteristic fragments and molecular ions in its mass spectra.

QUANTITATIVE ANALYSIS

Peak identities in the FID gas chromatograms were assigned by referring to the corresponding GC–MS chromatograms and semiquantitative values determined for the level of such compounds in the original sample based on peak heights relative to phthalate esters, fatty acid esters, and *n*-alkanes as external standards. The use of internal standards was not practical due to the complexity of the chromatograms. Compound enhancement (spiking) experiments were not feasible and consequently the efficiency of recovery is unknown. However, in other studies (Strachan 1976), these conditions have been shown to be optimal for the extraction of water samples. Analytical values reported here represent minimum values only and in the case of more volatile substances, actual levels may be appreciably higher than observed due to loss during evaporation of the extracts. Under the conditions employed, the approximate detection limits were 0.1 μg/ℓ in water, 10 μg/g dry weight of seston, 0.1 μg/g dry weight of sediment, and 1 μg/g dry weight of macrophyte tissue. For water samples taken near the discharge, the total material which eluted from the gas chromatographic column in defined peaks constituted 10–40% by weight of the chloroform extractable material. For more distant water samples, the corresponding value is 1–5% reflecting the generally lower levels of gas chromatographable material in these samples.

Analyses were complicated by the presence of ethyl esters of acids as artifacts in many of the methylated extracts. The source of these ethyl esters was determined to be the chloroform which contains ethanol as a stabilizer. Heating pure palmitic, stearic, and dehydroabietic acids for 22 h in some samples of chloroform resulted in formation of detectable quantities of the corresponding ethyl esters. Keith (1975) has also observed ethyl palmitate in extracts of kraft mill wastewaters where chloroform was used in the extraction procedure. For those samples in which this occurred, the combined concentration of the methyl and ethyl esters was used to calculate the concentration of the parent acid.

PREPARATION OF METHYL 7-OXODEHYDROABIETATE

7-oxodehydroabietic acid was prepared by potassium permanganate oxidation of dehydroabietic acid (300 mg) at room temperature for 5 min (Pratt 1951). A portion of the product in diethyl ether was methylated with ethereal diazomethane and purified to homogeneity by preparative thin layer chromatography on silica gel. The nuclear magnetic resonance spectrum (CCl_4) was consistent with the assigned structure and in agreement with published data (Biellmann et al. 1973a). The 2,4-dinitrophenylhydrazone melted at 184–185°C (corrected); lit, 185 C (Defaye-Duchateau 1964), 184.5–185.5°C (Ritchie et al. 1953).

Results and Discussion

To determine which compounds identified in Nipigon Bay samples were mill-related, it was necessary to identify as many compounds as possible in the mill effluent itself. On July 19 and 20, samples of the three mill effluent streams were collected and processed without filtration. Fifteen compounds were identified in concentrations between 2.5 and 1500 mg/ℓ (Table 1). All were methylated derivatives of phenols, fatty acids, and resin acids with the exception of dioctyl phthalate and the artifact, ethyl palmitate. As a group, the resin acids occurred in the highest concentrations. Similarity indices of 0.5 or greater in all but one case (methyl neobietate, 0.44), indicated that a high degree of confidence could be placed in the identification where this was the method used. Six of the compounds were identified in the mill effluent found in samples from the bay (Tables 2 and 3). The parent compounds before methylation are: acetovanillone (3, 4-dimethoxyacetophenone after methylation), sandaracopimaric acid, 7-oxodehydroabietic acid, dehydroabietic acid, palmitic acid, and dioctyl phthalate. The structure of these compounds, and others mentioned in this paper, are given in Fig. 2.

Three of the structural assignments in Table 1 require elaboration since their spectra do not appear in the spectral search systems. 3,4,5-Trichloroveratrole (Ib in Fig. 2) was assigned by

TABLE 1. Compounds identified in derivatized chloroform extracts of mill effluent streams.

Similarity index[a]	Compound	Concentration (μg/ℓ) in effluent streams: Clarifier	Low suspended solids	Uncontaminated	Concentration (μg/ℓ) in total effluent[b]
—[c]	Dichloroveratrole		30		7
0.54	3,4-dimethoxyacetophenone		25		6
—[c]	3,4,5-trichloroveratrole		11		2.5
0.87	Methyl palmitate	55[d]	40[d]	45[d]	50[d]
0.73	Ethyl palmitate				
0.50	Methyl linolenate	85	18	18	60
0.86	Methyl linoelaidate	220	15	17	150
0.59	Methyl stearate			75	9
0.73	Methyl sandaracopimarate	230	60	55	170
0.64	Methyl isopimarate	530	120	100	380
0.61	Methyl dehydroabietate	1750	410	410	1300
0.74	Methyl abietate	2200	150	55	1500
0.44	Methyl neoabietate	60	9		40
0.51	Methyl 9,10-dihydroxystearate		12		3
—[c]	Methyl 7-oxodehydroabietate	30	3	20	25
0.60	Dioctyl phthalate	7	30	20	15

[a] Explained in text.

[b] Calculated values based on a weighted average for the constituent streams where the relative volume flows are: clarifier, 65%; low suspended solids, 23%; uncontaminated, 12%.

[c] Spectra of these compounds were not available in the mass spectral library searched.

[d] For the methyl and ethyl esters combined; the ethyl ester is an artifact of the isolation procedure.

comparison of our mass spectrum with the published spectrum of this compound found as the trichloroguaiacol isomers (Ia) in kraft bleaching effluent (Rogers and Keith 1974). The spectra are qualitatively very similar with minor differences in relative intensities. The structure for dichloroveratrole (II) is assigned without specifying the isomer and is done on the basis of spectral similarity to 3,4,5-trichloroveratrole, with important fragment ions being shifted lower by 34 amu. While 3,4,5-trichloroveratrole has an isotope cluster at m/e 240, 242, 244 for the molecular ion ($C_8H_7Cl_3O_2$) and the base peak at m/e 162, dichloroveratrole has an isotope cluster at m/e 206, 208, 210 for the molecular ion ($C_8H_8Cl_2O_2$) and the base peak at m/e 128. Similar loss patterns can be observed in both spectra for M-15 ($-CH_3$), M-43 ($-CH_3$, $-CO$), and M-78 ($-CH_3$, $-CO$, $-Cl$) the base peak. The mass spectrum is shown in Fig. 3A.

The GC retention time and mass spectrum of the third compound, methyl 7-oxodehydroabietate, were the same as those of authentic material. The mass spectrum (Fig. 3B) shows a strong molecular ion at m/e 328 ($C_{21}H_{28}O_3$) and a base peak at m/e 253 in agreement with the proposed fragmentation scheme of Enzell and Wahlberg (1969) for esters of dehydroabietic acid. By analogy with the other resin and fatty acids (Fox 1977), it is presumed that this material occurred as the free acid, 7-oxodehydroabietic acid (VIa), and was observed in both effluent and water samples. To our knowledge this is the first time that this compound has been identified in kraft mill effluent or in environmental samples. Quantitation of this compound was somewhat more difficult because it was not fully resolved from dioctyl phthalate under the GC conditions employed.

The di- and trichloroveratroles and the dihydroxystearate observed can all be attributed to processes in the bleachery, the effluent of which is part of the "low suspended solids" stream. The dimethoxyacetophenone is present also in this stream but should have been observed in the "clarifer" extract as well since this stream received the effluent from the digestors which would be expected to contain the parent compound as a lignin breakdown product. Its absence cannot be satisfactorily explained at present. Most of the remaining compounds were present in all three streams but due to the higher flow and concentrations of the "clarifier" line, this is the major source of the overall mill loading of these compounds.

Of the 15 compounds identified, 9 were found only in the effluent. It was concluded that either they are not persistent, e.g. abietic acid, or are present in the effluent in such small quantities as to be undetectable in the water even at moderate dilutions, e.g. trichloroguaiacol isomers (Ia). Pos-

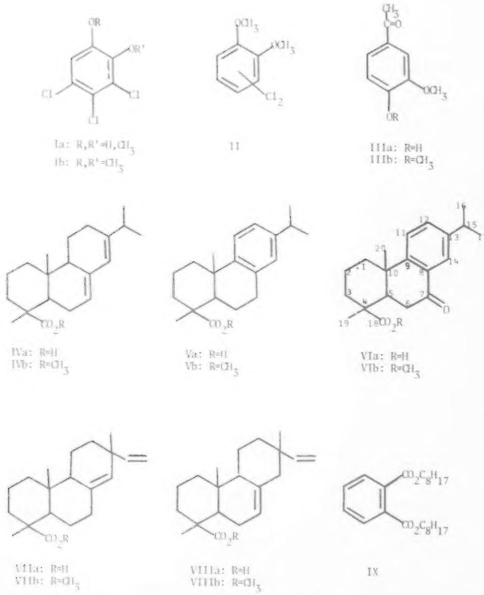

FIG. 2. Structural formulae of kraft mill related compounds. Ia, trichloroguaiacol isomers; Ib, 3,4,5-trichloroveratrole; II, dichloroveratrole; IIIa, acetovanillone; IIIb, 3,4-dimethoxyacetophenone; IVa, abietic acid; Va, dehydroabietic acid; VIa, 7-oxodehydroabietic acid; VIIa, sandaracopimaric acid; VIIIa, isopimaric acid; IX, dioctyl phthalate.

sible exceptions to this are the C_{18} unsaturated fatty acids, linolenic, and linoelaidic, which were identified as the methyl esters in extracts of the effluent. Peaks having the same retention times appeared in chromatograms of several extracts of water, seston, sediment, and macrophytes but it was difficult to confirm their identities in these samples since their mass spectra gave variable base peaks and highest masses and the molecular ions were only occasionally observed. Leach and Thakore (1973) have shown that C_{16} and C_{18} unsaturated fatty acids contribute some of the toxicity of kraft mill unbleached whitewater to fish. In view of the difficulties mentioned above and the probable biosynthetic origin of significant quantities of these substances in the receiving waters, further confirmation was not attempted.

In general, mill-related compounds were found most often in water and sediment samples and less frequently in seston samples. The latter was possibly due either to the high detection limits or to the fact that such compounds do not accumulate in sestonic material. Extracts of macrophyte samples, identified as *Potamogeton richardsonii* and *Potamogeton vaginatus*, contained a limited number of fatty acids and several other compounds which appeared to be plant diterpenes and sterols but no mill-related substances. This supports the hypothesis that such compounds do not accumulate appreciably.

Three mill-related compounds (Table 2) were moderately persistent. Acetovanillone and sandaracopimaric acid were observed at levels of 0.3 and 2.2 μg/ℓ, respectively, in one water sample collected 1.0 km from the effluent discharge (station 2). 7-oxodehydroabietic acid was identified in five water samples at trace concentrations to 9 μg/ℓ. This latter value is probably not representative as this location coincided with the edge of the visual effluent plume at the time of sampling. No clear trend of decreasing concentration of this compound with increasing distance from the effluent discharge can be seen from the data, due to the limited number of observations. This compound was also detected by Fox (1977) in effluent plume samples.

Palmitic acid was the most widely distributed mill-related compound (Table 3), although the significance of this is uncertain due to natural sources within the bay. Dioctyl phthalate was found in 10 water samples, one seston and one sediment sample (Table 3). Accidental contamination is a serious problem in analysis of environmental samples for phthalate esters. However, extensive precautions were taken to protect against contamination from identifiable sources of phthalate esters. It is reasonable, therefore, to conclude that the mill effluent is at least one source of dioctyl phthalate in Nipigon Bay and that this material is widely distributed throughout the study area.

Dehydroabietic acid is the most significant mill-related compound observed in Nipigon Bay samples. It is added to the receiving waters in large quantities and was found in a majority of samples (Table 3). The effluent concentration was in ex-

TABLE 2. Levels of acetovanillone (IIIa), 7-oxodehydroabietic acid (VIa), and sandaracopimaric acid (VIIa) in water samples.

Distance from source (*km*)	Station	Concentration (μg/ℓ)		
		IIIa	VIa	VIIa
0	Effluent	6	25	170
1.0	2	0.3	0.4	2.2
1.0	15[a]		9	
1.7	16		0.6	
1.8	5		trace	
4.7	9		0.1	

[a]At the time of sampling this location coincided with the edge of the visual effluent plume.

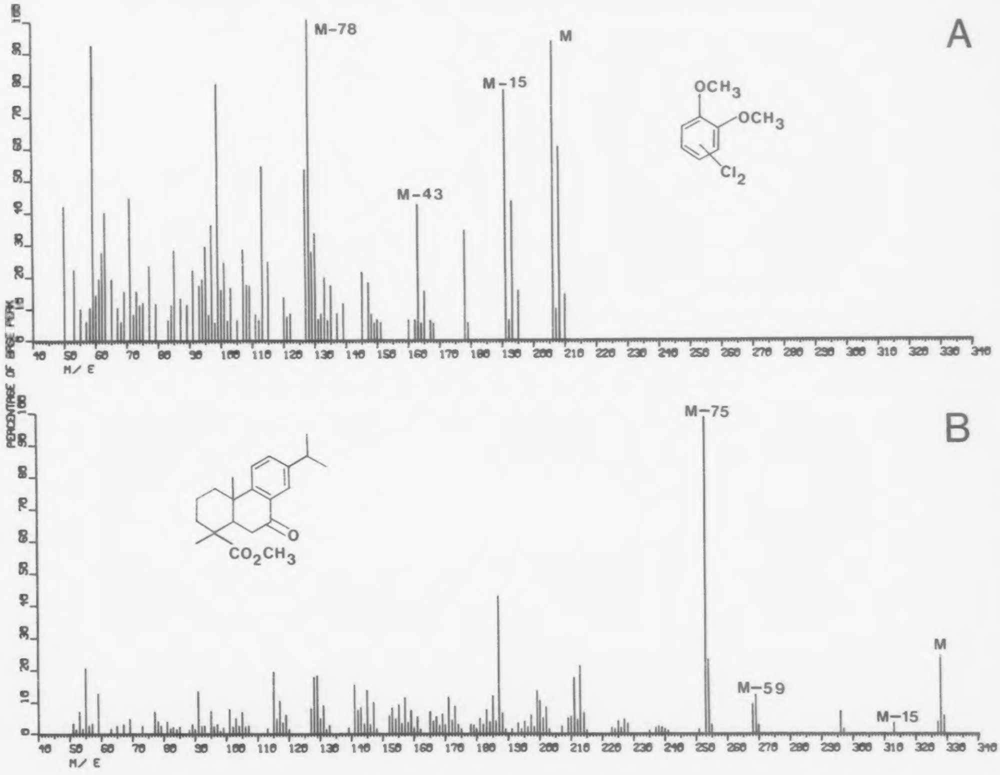

FIG. 3. Mass spectra of dichloroveratrole (A) and of 7-oxodehydroabietic acid (B).

cess of 1 mg/ℓ on the one occasion when the mill effluent streams were sampled during this study. Fox (1977) observed similar or higher concentrations on several sampling dates. The only other identifiable input of dehydroabietic acid to the study area was the Nipigon River (see Fig. 1 and Table 3, station 14). Due to the high loading and persistence of this compound it is a good indicator of the distribution and fate of persistent organic compounds entering these receiving waters from the mill effluent.

The results in Table 3 for concentrations of dehydroabietic acid in water at 5 m depth showed approximately 8 μg/ℓ for the region 1–2 km from the discharge but not within the plume. Somewhat lower values (average 0.4 μg/ℓ) were observed in the region beyond 2 km from the effluent discharge where it appears that a background level is reached. Fox (1977) found similar levels in the 2 km region outside the plume and concluded that the decreasing concentration of dehydroabietic acid in the effluent plume with increasing distance from the outfall was due mainly to dilution. Water body movement in the area appears to be complex (Kelso et al. 1977; Polak and Palmer 1977; Rokosh et al. 1977) and a water quality survey[2] undertaken at the same time indicated that, to a first approximation, no concentration gradients outside the plume could be attributed to the mill. Based on the results in the present study, it is not possible to state that dilution is the primary mechanism responsible for the low levels of dehydroabietic acid beyond the 2 km region. There is some indication that other processes are possible, particularly sedimentation and degradation.

Dehydroabietic acid was observed in each of the four sediment samples examined. The highest level (150 μg/g dry weight) was observed in a

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[2] The survey was undertaken (Brownlee and Strachan 1975) using essentially the same sampling pattern as shown in Fig. 1 where chlorophyll-*a*, adenosine triphosphate, particulate carbon, nitrogen and phosphorus forms, seston organic and inorganic weights and dissolved nutrients were measured.

TABLE 3. Levels of palmitic acid (X), dehydroabietic acid (Va), and dioctyl phthalate (IX) in water, seston, and sediment samples.

Distance from source (*km*)		0	1.0	1.0	1.6	1.7	1.8	2.2	2.5	3.0	3.1	3.6	3.9	4.7	5.7	3.0	6.8
Station		Effluent	2	15	4	16	5	3	7	6	17	12	10	9	8	14	19
Concentration	*X*	50	0.5	1.5[a]	0.1	1	0.2	0.2	0.1	0.5	0.4	0.4	0.7	0.2	0.6	0.9	0.2
in water	*Va*	1300	15	100[a]		10	0.4		0.04	0.3	0.7	0.1	0.6	2	0.08	0.2	0.1
(μg/ℓ)	*IX*	15	1	55[a]	0.1	2						1.5	1	0.6	0.3	0.5	0.3
Concentration	*X*			550[a]	500	750	700	1000	1500	150		1000	500	1300	2000	2000	400
in seston	*Va*			60[a]			40			7			35				
(*μg/g dry weight*)	*IX*							Trace									Trace
Concentration	*X*		100												0.3	1	3
in sediment[b]	*Va*		150												0.1	2	0.3
(*μg/g dry weight*)	*IX*															0.7	

[a] At the time of sampling this location coincided with the edge of the visual effluent plume. These values are similar to plume concentrations at this distance from the effluent discharge (Fox 1977).

[b] Sediment samples were collected at Stations 2, 8, 14, and 19 only.

sample collected 1 km from the effluent discharge (Station 2, Fig. 1). Considerably lower levels (0.1–2 μg/g dry weight) were observed 3–7 km from the discharge. Dehydroabietic acid was observed in four seston samples at 7–60 μg/g dry weight. These were collected at locations roughly on a line from near Burnt Island to 1 km southeast of the effluent discharge (Fig. 1, Stations 10, 6, 5, and 15). Dehydroabietic acid in particulate material in the effluent may settle and accumulate in the sediment near the discharge. Alternatively, dissolved dehydroabietic acid may undergo accretion to particulate material which then settles out. Dehydroabietic acid in sediments of the area is discussed in more detail in a accompanying paper (Brownlee et al. 1977).

Degradation of dehydroabietic acid to 7-oxodehydroabietic acid may also be a removal process. Microbiological studies on the utilization of dehydroabietic acid (or its methyl ester) in pure cultures have shown that oxidation occurs first in the 3- and/or 7- position followed by hydroxylation of the aromatic ring (Brannon et al. 1968; Biellmann et al. 1973a, 1973b). No compounds corresponding to other degradation products of dehydroabietic acid were observed in our samples. The oxidized acid found in the mill effluent may have been present in the wood used by the mill or produced from dehydroabietic acid during pulping or bleaching. Further quantities of 7-oxodehydroabietic acid may have been produced by degradation of the parent acid in the water column as indicated by an increased proportion of the 7-oxo acid at locations remote from the discharge.

Of the limited number of mill-related compounds found outside the effluent plume, dehydroabietic acid and 7-oxodehydroabietic acid should be studied further. Dehydroabietic acid was found over an area of at least 25 km² in water and sediment and in a few seston samples. Water concentrations at or exceeding the acute toxicity levels for fish in fresh water (96 h LC50, 0.5–2 mg/ℓ, Rogers 1973; Leach and Thakore 1974; Rogers et al. 1975) occur at the discharge and in the effluent plume at distances less than 0.5 km from the discharge (Fox 1977). Dehydroabietic acid concentrations of 500 μg/ℓ have been shown to inhibit phytoplankton primary productivity (Moore and Love 1977) and in another study, Kaiser (1977) has identified dehydroabietic acid in the skin of a white sucker (*Catostomus commersoni*) captured approximately 3 km from the discharge. The findings of this study, that concentrations of approximately 1% of acutely toxic levels of dehydroabietic acid can occur in the water at distances of up to 1.7 km from the discharge, suggest that investigations should be undertaken on the sublethal effects of dehydroabietic acid on freshwater aquatic organisms.

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Biellmann, J. F., G. Branlant, M. Gero-Robert, and M. Poiret. 1973a. Bacterial degradation of dehydroabietic acid by *Flavobacterium resinovorum*. Tetrahedron 29: 1227–1236.

1973b. Bacterial degradation of dehydroabietic acid by *Pseudomonas* and *Alcaligenes*. Tetrahedron 29: 1237–1241.

Brannon, D. R., et al. 1968. Hydroxylation of some dehydroabietanes with *Corticium sasakii*. J. Org. Chem. 33: 4462–4466.

Brownlee, B., M. E. Fox, W. M. J. Strachan, and S. R. Joshi. 1977. Distribution of dehydroabietic acid in sediments adjacent to a kraft pulp and paper mill. J. Fish. Res. Board Can. 34. (This issue)

Brownlee, B., and W. M. J. Strachan. 1975. A chemical–biochemical examination of the Red Rock-Nipigon Bay area. Can. Cent. Inland Waters. (Unpublished rep.)

Das, B. S., S. G. Reid, J. L. Betts, and K. Patrick. 1969. Tetrachloro-*o*-benzoquinone as a component in bleached kraft chlorination effluent toxic to young salmon. J. Fish. Res. Board Can. 26: 3055–3067.

Defaye-Duchateau, G. 1964. Oxidations in the dehydroabietic acid series. Bull. Soc. Chim. Fr. 1469–1473.

Enzell, C. R., and I. Wahlberg. 1969. Mass spectrometric studies of diterpenes. Acta Chem. Scand. 23: 871–891.

Fox, M. E. 1977. Persistence of dissolved organic compounds in kraft pulp and paper mill effluent plumes. J. Fish. Res. Board Can. 34. (This issue)

Heller, S. R. 1972. Conversational mass spectral retrieval system and its use as an aid in structure determination. Anal. Chem. 44: 1951–1961.

Hertz, H. S., R. A. Hites, and K. Biemann. 1971. Identification of mass spectra by computer-searching a file of known spectra. Anal. Chem. 43: 681–691.

Hoyland, J. R., and M. B. Neher. 1974. Implementation of a computer-based information system for mass spectral identification. U.S. Environ. Prot. Agency, EPA-660/2-74-048: 43 p.

Kaiser, K. L. E. 1977. Organic contaminant residues in fishes from Nipigon Bay, Lake Superior. J. Fish. Res. Board Can. 34. (This issue)

Keith, L. H. 1975. Analysis of organic compounds in two kraft mill wastewaters. U.S. Environ. Prot. Agency Publ. EPA-660/4-75-005: 99 p.

Keith, L. H., and S. H. Hercules. 1973. Environmental applications of advanced instrumental analyses. Assist. proj. FY 69-71. U.S. N.T.I.S. PB Rep. 222938/3: 92 p.

Kelso, J. R. M., C. K. Minns, and R. J. P. Brouzes. 1977. Pulp and paper mill effluent in a freshwater environment. J. Fish. Res. Board Can. 34. (This issue)

Leach, J. M., and A. N. Thakore. 1973. Identification of the constituents of kraft pulping effluent that are toxic to juvenile coho salmon (*Oncorhynchus kisutch*). J. Fish. Res. Board Can. 30: 479–484.

1974. Isolation of the toxic constituents of kraft pulp mill effluents. CPAR Proj. 11. Can. For. Serv.

1975. Isolation and identification of constituents toxic to juvenile rainbow trout (*Salmo gairdneri*) in caustic extraction effluents from kraft pulpmill bleach plants. J. Fish. Res. Board Can. 32: 1249–1257.

Maenpaa, R., P. Hynninen, and J. Tikka. 1968. On the occurrence of abietic and pimaric acid type resin acids in the effluents of sulphite and sulphate pulp mills. Pap. Timber 50: 143–150.

Marier, J. R. 1973. The effects of pulp and paper wastes, with particular attention to fish bioassay procedures for assessment of harmful effects. NRC (Nat. Res. Coun. Can.) 13501: 33 p.

Moore, J. E., and R. Love. 1977. Effect of a pulp and paper mill effluent on the productivity of periphyton and phytoplankton. J. Fish. Res. Board Can. 34. (This issue)

Polak, J. and, M. D. Palmer. 1977. Concentration pattern of chemical constituents in a paper mill's effluent plume: dynamics and model. J. Fish. Res. Board Can. 34. (This issue)

Pratt, Y. T. 1951. Derivatives of dehydroabietic acid. J. Am. Chem. Soc. 73: 3803–3807.

Ritchie, P. F., T. F. Sanderson, and L. F. McBurney. 1953. The oxidation of methyl dehydroabietate by molecular oxygen. J. Am. Chem. Soc. 75: 2610–2612.

Rogers, I. H. 1973. Isolation and chemical identification of toxic components of kraft mill wastes. Pulp Pap. Mag. Can. 74: T303.

Rogers, I. H., et al. 1975. Fish toxicants in kraft effluents. Tappi 58: 136–140.

Rogers, I. H., and L. H. Keith. 1974. Organochlorine compounds in kraft bleaching wasters. Identification of two chlorinated guaiacols. Fish. Mar. Serv. Res. Dev. Tech. Rep. 465: 21 p.

Rokosh, D. A., S. S. Rao and A. A. Jurkovic. 1977. Extent of effluent influence on lake water determined by bacterial population distributions. J. Fish. Res. Board. Can. 34. (This issue)

Shumway, D. F., and J. R. Palensky. 1973. Impairment of flavour of fish by water pollutants. U.S. Environ. Prot. Agency EPA-R3-73-010: 79 p.

Strachan, W. M. J. 1976. Chloroform-extractable organic compounds in the International Great Lakes, chap. 28. *In* L. H. Keith [ed.] Identification and analysis of organic pollutants in water. Ann Arbor Science, Ann Arbor, Mich.

Thomas, N. A. 1973. Assessment of fish flesh tainting substances. Biological methods for the assessment of water quality. Am. Soc. Test. Mat. Spec. Tech. Publ. 528: 178–193.

Distribution of Dehydroabietic Acid in Sediments Adjacent to a Kraft Pulp and Paper Mill[1]

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Brownlee, B., M. E. Fox, W. M. J. Strachan, and S. R. Joshi. 1977. Distribution of dehydroabietic acid in sediments adjacent to a kraft pulp and paper mill. J. Fish. Res. Board Can. 34: 838–843.

Sediments adjacent to a kraft pulp and paper mill on western Nipigon Bay, Lake Superior, were examined for resin acids. Dehydroabietic acid was the predominant resin acid with surficial concentrations of less than 5–100 $\mu g/g$.

The areal distribution indicated the mill to be the primary source of this compound. Depth profiles of the acid and core dating by ^{210}Pb methods enabled the calculation of a mean sediment accumulation rate of $0.11\ cm \cdot yr^{-1}$ and a half-life for the disappearance of dehydroabietic acid in the sediments of approximately 21 yr. A half-life of 0.12 yr was estimated for this compound in the water column. It appears, therefore, that the primary removal mechanism of dehydroabietic acid is degradation in the water column.

Brownlee, B., M. E. Fox, W. M. J. Strachan, and S. R. Joshi. 1977. Distribution of dehydroabietic acid in sediments adjacent to a kraft pulp and paper mill. J. Fish. Res. Board Can. 34: 838–843.

Les auteurs ont examiné les sédiments du voisinage d'un moulin de pâte et de papier kraft de la baie Nipigon occidentale, lac Supérieur, en vue d'y détecter des acides résineux. L'acide déshydroabiétique est l'acide résineux prédominant, avec des concentrations superficielles comprises entre moins de 5 et 100 $\mu g/g$.

La distribution en superficie indique que le moulin est la source première de ce composé. Les profils bathymétriques de l'acide et des mesures d'âge de carottes par des méthodes au ^{210}Pb donnent un taux moyen d'accumulation du sédiment de $0.11\ cm \cdot an^{-1}$ et une période d'environ 21 ans pour la disparition de l'acide déshydroabiétique dans les sédiments. Nous avons estimé à 0.12 an la période de ce composé dans la colonne d'eau. Il semble donc que le mécanisme principal d'enlèvement de l'acide déshydroabiétique est la dégradation dans la colonne d'eau.

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Introduction

Resin acids are important components of wood which are extracted from the cellulose fiber during processing in the kraft pulp industry. While these diterpene acids, together with fatty acids, represent only a few per cent of the weight of the wood (Enos et al. 1968), the quantities which can be released to the environment are such that concentrations in effluents (Dymond and Delaporte 1952; Maenpaa et al. 1968; Fox 1977; Brownlee and Strachan 1977) may reach toxic levels (Leach and Thakore 1973; Rogers et al. 1975; Davis and Hoos 1975). Even when diluted by receiving waters, concentrations of these compounds may still be sufficient to exert chronic effects on the aquatic community.

Most of the resin acids are apparently readily degraded (Hemingway and Greaves 1973; Rogers and Mahood 1974; Spencer et al. 1974) but, because of the stability conferred by its aromatic ring structure, dehydroabietic acid is likely to be more persistent than the other resin acids. Examination for the products of microbial degradation of dehydroabietic acid has been the subject of several laboratory studies (Biellmann et al.

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

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1973; Brannon et al. 1968; Levinson et al. 1968) which showed that this compound can be metabolized. There are, however, indications that this resin acid is persistent in western Nipigon Bay (Brownlee and Strachan 1977) where the effluent from a kraft pulp mill discharges at Red Rock, Ont. In this same study, it was apparent that the concentrations of dehydroabietic acid in the waters of the bay were insufficient to account for the net inputs to the area and that some processes, other than dilution were operating, e.g. sedimentation and degradation.

Consequently, an examination was undertaken of a number of surface sediment samples from the western part of Nipigon Bay to determine the extent of dehydroabietic acid accumulation. In addition to the distribution studies, the rate of disappearance of dehydroabietic acid was determined in several sediment cores to give some indication of the persistence of this compound under environmental conditions. The interpretation of chemical profiles in freshwater surficial sediments required a knowledge of recent sedimentation rates. The use of ^{210}Pb for this purpose has recently been evaluated (Krishnaswamy et al. 1971) and this was the method employed in dating the core sediments.

Materials and Methods

SEDIMENT SAMPLES

Grab samples of surface sediments (0–1 cm) and duplicate sediment cores were obtained (Sandilands 1977) from which complete details of sampling sites, collection methods, and sediment description can be obtained.

Duplicate cores from five sites (stations 3, 13, 20, 24, and 35 in Fig. 1) were stored in the dark at 4 C and subsequently extruded. Segments from 0 to 1, 1 to 2, 2 to 3, 5 to 6, 8 to 9, and 15 to 16 cm from one core at each site were analyzed for resin acids. The other core was used for dating. In addition, the 17 surface sediment samples (Fig. 1) which were preserved in a similar manner to that of the cores, were subsampled (approximately 50 g) and analyzed.

EXTRACTION OF RESIN ACIDS FROM SEDIMENTS

The wet surface sediment subsamples and the core segments were weighed into preextracted cellulose Soxhlet thimbles and extracted with 200 ml of residue-free acetone for 3 h. The resulting extract was evaporated to a wet slurry and reextracted with residue-free diethyl ether (10 ml). The ether solution was evaporated to 1 ml in a Kuderna Danish evaporator and methylated with diazomethane. This reagent methylates dehydroabietic acid with 95% yield (Webb et al. 1973). The surface sample from station 22, which had the highest observed level of dehydroabietic acid, was reextracted in the Soxhlet apparatus for a further 3 h to check on the efficiency of the initial extraction. No additional quantities of resin acids were observed in this second extraction. No difference in dehydroabietic acid concentration was observed (within 5%) with identical subsamples stored as above or freeze-dried, indicating the stability of this acid in the wet samples.

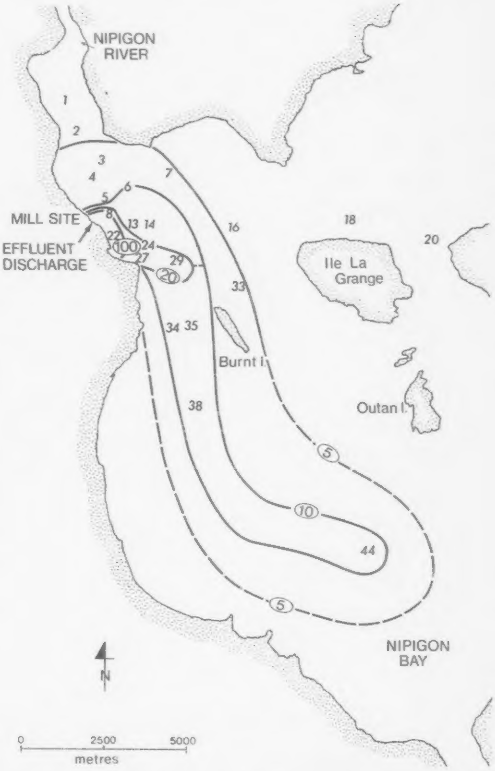

FIG. 1. Distribution of dehydroabietic acid in surface sediments of western Nipigon Bay. Contour levels are given as μg/g (dry weight) and are indicated by circled numbers; other numbers represent station sites.

ANALYSES OF RESIN ACIDS

Initial examination for resin acids in the sediment extracts as their methyl ester derivatives, was by gas–liquid chromatography (GC) using a 1.8 m × 3 mm 3% OV-1 packed column operating under the same conditions as were employed in the examination of water samples (Brownlee and Strachan 1977). Later investigations employed a 15 m OV-1 SCOT (Support Coated Open Tubular) column, programmed from 170 to 225°C at 2°C/min in a Perkin-Elmer 900 gas chromatograph equipped with a single flame ionization detector at 250°C. The injection port, equipped with a splitter and solvent vent valve, was also at

250°C. Carrier gas was helium at a column inlet pressure of 2.8 kg/cm^2.

Quantitative determination of the resin acids was based on GC peak heights from the packed column chromatograms, using dehydroabietic acid as an external standard. The total concentration of dehydroabietic plus an unresolved abietanoic acid isomer was determined in this manner and the individual contributions were etsimated from the ratio of their peak heights obtained with the SCOT column (Fig. 2). An abietenoic acid isomer was adequately resolved with the packed column. All such determinations were expressed as dry weight concentrations.

Similar GC conditions to those employed by Zinkel et al. (1971) were used with the packed column to indicate identities in most of the samples. The compounds named in Fig. 2 were confirmed from their mass spectra obtained under the packed column conditions. The mass spectra of the abietanoic, dehydroabietic and eicosanoic acid esters were obtained by examination and spectral subtraction of the partially resolved GC peak. Other spectra were obtained directly.

SEDIMENTATION RATES

Cores from stations 3, 13, and 35 were sectioned at 0.5 cm intervals and analyzed for excess ^{210}Pb and ^{137}Cs contents, using the methods described in detail by Joshi and Durham (1976).

Results and Discussion

Preliminary examination of the sediment extracts was done on the packed column and on the GC–MS. The observation of unexpected mass fragments in the mass spectrum of the GC peak corresponding to dehydroabietic acid led to further examination on the SCOT column. This improved the GC resolution and showed, in addition to the anticipated dehydroabietic acid, an abietanoic and an abietenoic acid (Fig. 2), both of which were absent from water samples from the area. Also present were abietic acid and pimaric acid. However, the quantitative estimation of these latter two resin acids was not possible due to the presence of unresolved eicosanoic acid and another unidentified resin acid, respectively.

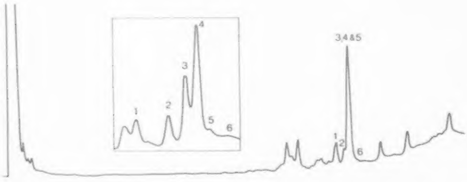

FIG. 2. Gas chromatogram of methylated extract of surface sediments from station 22 on a 1.8 m packed column. Inset shows the increased resolution in the resin acid region obtained with a 15 m SCOT column. Identified peaks show methyl esters of: 1, pimaric acid; 2, abietenoic acid; 3, abietanoic acid; 4, dehydroabietic acid; 5, eicosanoic acid; 6, abietic acid.

Dehydroabietic acid in the surface sediments showed a well-defined pattern of elevated concentrations near the effluent discharge (Fig. 1, Table 1) with the highest value being approximately 20 times the local background level of less than 5 μg/g. The zone of elevated concentrations extended in a southeasterly direction following the deep channel toward Nipigon Strait and conformed to the pattern of organic carbon in these sediments (Sandilands 1977). Even at 15 km towards Nipigon Strait, a dehydroabietic acid concentration of twice the Nipigon Bay background level was still observed. Concentrations of 1–2 μg/g were also observed in the Nipigon River mouth, indicating that the mill is the primary source of the elevated level of dehydroabietic acid in these sediments.

The abietanoic and abietenoic acids showed qualitatively similar distribution patterns to those of dehydroabietic acid although their levels were lower and tended to decline more rapidly with increasing distance from the mill. The ratio of dehydroabietic acid to the abietanoic plus abietenoic acids was lower near the mill (approximately 1:1) than further away (approximately 2:1) and indicated that these two acids were not derived from degradation of the dehydroabietic acid in the reducing sediments. Since they were not observed in the effluent itself (Brownlee and

TABLE 1. Concentrations of dehydroabietic, an abietanoic and an abietenoic acid in surface sediments of western Nipigon Bay.

Sample station	Dehydroabietic acid ($\mu g/g$)	Abietanoic acid ($\mu g/g$)	Abietenoic acid ($\mu g/g$)
1	1.5	0.5	0.4
2	4	1	1
4	6	1	1
5	7	2	2
6	11	3	3
7	8	2	4
8	99	29	47
14	16	4	4
16	4	1	1
18	2	0.5	0.5
22	101	66	31
27	25	16	9
29	30	11	10
33	8	1	2
34	14	4	3
38	19	4	5
44	10	2	2

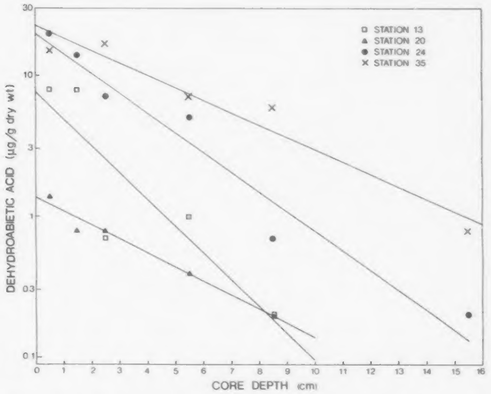

FIG. 3. Dehydroabietic acid depth profiles for sediment cores of western Nipigon Bay.

Strachan 1977; Fox 1977), it may be that they are derived from abietic acid which was reported there at relatively high levels (1.5 mg/ℓ).

Dehydroabietic acid concentration–depth profiles are shown semilogarithmically in Fig. 3 for the four analyzed cores; and the data, together with the least squares slopes and correlation coefficients, are given in Table 2. Good linearity between log concentration and depth was observed in these recent sediments; even for the poorest correlation, in core 13, the correlation coefficient of 0.88 is significant at the 98% confidence level. The slopes indicate that there is a trend towards a more rapid disappearance of dehydroabietic acid in the vicinity of the mill which may be the result of higher levels of microbial activity in this part of the bay (Rokosh et al. 1977).

As with the surface pattern, the abietanoic and abietenoic acid profiles in the cores showed qualitatively similar behavior to that of the dehydroabietic acid but the lower levels and fewer observations of these two compounds made further investigation impractical.

Data for the ^{210}Pb profiles for stations 3, 13, and 35 are shown in Fig. 4 and include the calculated dates for several segments in each core. Core 13, in comparison with cores 3 and 35, was deficient in ^{210}Pb activity and the sediment accumulation rate of 0.16 cm·yr^{-1} was significantly higher than at the other two stations where it was 0.07 and 0.10 cm·yr^{-1}, respectively. Also, at station 13, the ^{210}Pb profile showed significant anomalies around the years 1951 and 1957. This station is the closest to the mill outfall and consequently has been subjected to a variety of influences arising from process changes in the mill, particularly, an alteration in the location of the outfall (1969), the installation of partial primary treatment (1972), the cessation of log booming immediately north of the mill (1973), and the partial conversion to groundwood pulp (1948).

Dating from ^{137}Cs activity, measured on the same subsamples as the ^{210}Pb dating, was qualitatively in agreement with the ^{210}Pb time scale. Due to the greater accuracy of the latter method, only the dates obtained by the ^{210}Pb method were employed in this study.

Using the mean slope from the dehydroabietic acid concentration–depth plots, −0.13 log units·cm^{-1}, and the mean value for the sediment accumulation rates, 0.11 cm·yr^{-1}, and assuming constant loading, an estimate of 21 yr was obtained for the half-life of the disappearance of this substance in these sediments. Data are not available on historical inputs to the region and, consequently, it was not possible to ascribe the decrease to either microbial action or loading effects. Since the mill has increased its production since its inception in 1945, it is certain that dehydroabietic acid inputs have also increased and that the calculated half-life should therefore represent a minimum value.

This rate, however, is inadequate to account for the total sediment load when this is compared with the net loading. Total sediment load was estimated in the following manner. Areas corresponding to the several surface concentration contours in Fig. 1 were determined by cutting and weighing. No account was taken of areas represented by surface concentrations of less than 5 µg/g. Amounts of dehydroabietic acid in each of these contour areas were calculated using the appropriate core profile relationship down to the depth corresponding to an arbitrary level 1 µg/g and the mean surface concentration for the area. The results of these calculations are given in Table 3 where the total sediment load is estimated at 12,000 kg. Dehydroabietic acid inputs to and exports from the area can be determined from concentrations given by Brownlee and Strachan (1977) and Fox (1977) and from flows available in Kelso et al. (1977) and Polak and Palmer (1977). There is a net input to the receiving waters of approximately 340 kg/day of which 97% is derived from the mill. Comparing this figure with the 12,000 kg in the sediments, it would seem that the entire sediment load represents only some 35 days' net input to the bay which is considerably shorter than the calculated 21-yr half-life. Indeed, if the quantity accumulated in one year in the surface sediments, 350 kg, is compared with the net loading over one year, 125,000 kg, a degradation rate constant can be

TABLE 2. Resin acid concentrations and depth profiles in sediment cores of western Nipigon Bay.

Core and depth (*cm*)	Dehydroabietic acid: Concentration (*μg/g*)	Dehydroabietic acid: Log. conc'n.–depth slope [corr. coef] (*cm*$^{-1}$)	Abietanoic (*μg/g*)	Abietenoic (*μg/g*)
Station 13				
0–1	8		7	0.4
1–2	8		4	1.0
2–3	0.7	−0.19 [0.88]	0.3	0.2
5–6	1		ND[a]	ND
8–9	0.2		ND	ND
Station 20				
0–1	1.4		0.6	0.1
1–2	0.8		0.2	(0.05)
2–3	0.8	−0.10 [0.99]	0.2	0.1
5–6	0.4		ND	ND
8–9	0.2		ND	ND
Station 24				
0–1	20		13	5
1–2	14		10	4
2–3	7	−0.14 [0.98]	5	2
5–6	5		2	1
8–9	0.7		0.3	0.2
15–16	0.2		0.1	ND
Station 35				
0–1	15		9	4
2–3	17		9	4
5–6	7	−0.09 [0.97]	5	1.3
8–9	6		3	1.7
15–16	0.8		0.1	ND

[a] ND — not detected.

TABLE 3. Dehydroabietic acid load in sediments.

Contour level (*μg/g*)	Area (*km*^{2})	Mean surface concentration (*μg/g*)	Depth to 1 *μg/g* (*cm*)	Dehydroabietic acid load[a] (*kg*)
5–10	43	7	9[b]	4600
10–20(North)[c]	3.4	12	7	520
10–20(South)[c]	15.2	14	14	5800
20–100	1.8	25	11	760
>100	0.7	100	11[d]	400
				12080

[a] Derived using observed densities and moisture contents to produce dry weights from calculated volumes.

[b] The concentration–depth profile for core 20 was employed.

[c] This contour was divided as there were separate cores for the two regions.

[d] The concentration–depth profile for core 13 was employed.

estimated at 5.9 yr^{-1}, corresponding to a half-life of 0.12 yr for the surface sediment and water column. This is also much less than that obtained for the sediments and consequently, it must be concluded that the primary removal mechanism for dehydroabietic acid is degradation, probably bacterial, in the water column.

Since export of dehydroabietic acid bound to suspended material was not taken into account in the preceding calculation, the calculated half-life of 0.12 yr represents a minimum value. Dehydroabietic acid would seem to have a half-life of at least 6 wk which is close to the 8 wk value defined (International Joint Commission 1975) as indicative of persistence for organic compounds. As a consequence, studies are indicated

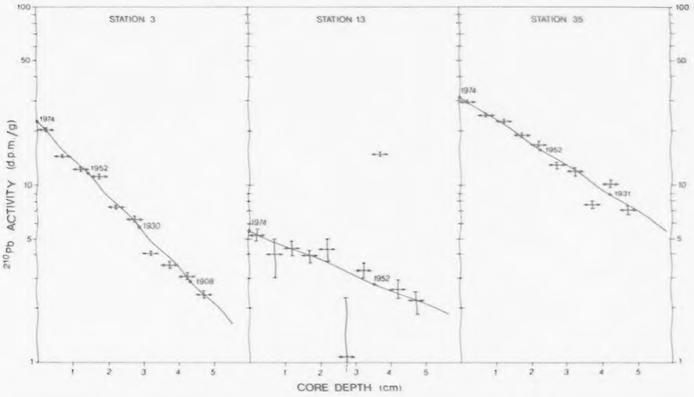

FIG. 4. Dating by ^{210}Pb activity of sediment cores of western Nipigon Bay.

on chronic effects to local sensitive aquatic organisms with a view to establishing safe levels for this compound.

BIELLMANN, J. F., G. BRANLANT, M. GERO-ROBERT, AND M. POIRET. 1973. Bacterial degradation of dehydroabietic acid by a *Pseudomonas* and an *Alcaligenes*. Tetrahedron 29: 1237.

BRANNON, D. R., ET AL. 1968. Hydroxylation of some dehydroabietanes with *Corticium sasakii*. J. Org. Chem. 33: 4462–4466.

BROWNLEE, B. G., AND W. M. J. STRACHAN. 1977. Distribution of some organic compounds in the receiving waters of a kraft pulp and paper mill. J. Fish. Res. Board Can. 34. (This issue)

DAVIS, J. C., AND R. A. W. HOOS. 1975. Use of sodium pentachlorophenate and dehydroabietic acid as reference toxicants for salmonid bioassays. J. Fish. Res. Board Can. 32: 411–416.

DYMOND, J. R., AND A. V. DELAPORTE. 1952. Pollution of the Spanish River, Ont. Dept. Lands For., Div. Res. Rep. 25: 106 p.

ENOS, H. I. JR., G. C. HARRIS, AND G. W. HEDRICK. 1968. Rosin and Rosin derivatives, p. 475–508. *In* A. Standen [ed.] Kirk-Othmer encyclopedia of chemical technology. 2nd ed. John Wiley and Sons, Inc., New York, N.Y.

FOX, M. E. 1977. Persistence of dissolved organic compounds in kraft pulp and paper mill effluent plumes. J. Fish. Res. Board Can. 34. (This issue)

HEMINGWAY, R. W., AND H. GREAVES. 1973. Biodegradation of resin acid sodium salts. Tappi 56: 189–192.

INTERNATIONAL JOINT COMMISSION. 1975. Great Lakes water quality board report for 1974. Append. A. Water Quality Objectives Subcommittee rep.: Persistent organic contaminants. 31–40.

JOSHI, S. R., AND R. W. DURHAM. 1976. Determination of ^{210}Pb, ^{226}Ra and ^{137}Cs in sediments. Chem. Geol. (In press)

KELSO, J. R. M., C. K. MINNS, AND R. J. P. BROUZES. 1977. Pulp and paper mill effluent in a freshwater environment. J. Fish. Res. Board Can. 34 (This issue)

KRISHNASWAMY, S., D. LAL, J. M. MARTIN, AND M. MEYBECK. 1971. Geochronology of lake sediments. Earth Planet. Sci. Lett. 11: 407–414.

LEACH, J. M., AND A. N. THAKORE. 1973. Identification of the constituents of kraft pulping effluent that are toxic to juvenile Coho salmon (*Oncorhynchus kisutch*). J. Fish. Res. Board Can. 30: 479–484.

LEVINSON, A. S., B. C. CARTER, AND M. L. B. TAYLOR. 1968. Microbial degradation of methyl dehydroabietate. Chem. Commun. 1344.

MAENPAA, R., P. HYNNINEN, AND J. TIKKA. 1968. On the occurrence of abietic and pimaric acid type resin acids in the effluents of sulphite and sulphate pulp mills. Pap. Timber 50: 143–150.

POLAK, J., AND M. D. PALMER. 1977. Concentration pattern of chemical constituents in a paper mill's effluent plume: dynamics and model. J. Fish. Res. Board Can. 34. (This issue)

ROGERS, I. H., ET AL. 1975. Fish toxicants in kraft effluents. Tappi 58: 136–140.

ROGERS, I. H., AND H. W. MAHOOD. 1974. Removal of fish-toxic organic solutes from whole kraft effluent by biological oxidation and the role of wood furnish extractives. Fish. Mar. Serv. Res. Dev. Tech. Rep. 434: 43 p.

ROKOSH, D. A., S. S. RAO, AND A. A. JURKOVIC. 1977. Extent of effluent influence on lake water determined by bacterial population distributions. J. Fish. Res. Board Can. 34. (This issue)

SANDILANDS, R. G. 1977. Effect of pulp mill effluent on the surficial sediments of western Nipigon Bay, Lake Superior. J. Fish. Res. Board Can. 34. (This issue)

SPENCER, J. F. T., G. D. SINCLAIR, AND N. R. GARDNER. 1974. Removal of resin acids from culture media and kraft mill effluents by yeasts and some other fungi. Can. J. Microbiol. 20: 1288–1290.

WEBB, R. G., A. W. GARRISON, L. H. KEITH, AND J. MCGUIRE. 1973. Current practice in GC-MS analysis of organics in water. U.S. Environ. Prot. Agency Publ. EPA-R2-73-277: 91 p.

ZINKEL, D. F., L. C. ZANK, AND M. F. WESOLOWSKI. 1971. Diterpene resin acids: A compilation of infrared, mass, nuclear magnetic resonance, ultraviolet spectra and gas chromatographic retention data (of the methyl esters). U.S. Dept. Agric. Publ., For. Serv., For. Prod. Lab. 191 p.

Extent of Effluent Influence on Lake Water Determined by Bacterial Population Distributions[1]

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ROKOSH, D. A., S. S. RAO, AND A. A. JURKOVIC. 1977. Extent of effluent influence on lake water determined by bacterial population distributions. J. Fish. Res. Board Can. 34: 844–849.

Populations of heterotrophic bacteria, total and fecal coliforms, and sulfur cycle bacteria were measured in a large body of water receiving the effluent of a pulp and paper industry. Elevated bacterial populations were detected near the effluent outfall but persistent populations, larger than those in unaffected lake water, extended as far as 19 km from the effluent outfall. This ability to detect influences to distances up to 19 km adds a new dimension to a description of a mixing zone receiving industrial effluents.

ROKOSH, D. A., S. S. RAO, AND A. A. JURKOVIC. 1977. Extent of effluent influence on lake water determined by bacterial population distributions. J. Fish. Res. Board Can. 34: 844–849.

Les bactéries hétérotrophes, les coliformes totaux et fécaux, ainsi que les bactéries du cycle du soufre ont été comptés dans une grande étendue d'eau recevant l'effluent d'une fabrique de pâte et de papier. Les populations bactériennes étaient élevées près du point de rejet de l'effluent et demeuraient plus grosses que celles que l'on trouve dans des eaux non polluées, jusqu'à 19 km du point de rejet. Le fait de pouvoir ainsi déceler des effets jusqu'à une telle distance ajoute une nouvelle dimension à la description des zones de mélange des effluents industriels.

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A study was undertaken to determine bacterial numbers in a large body of water enriched by the effluent of a pulp and paper mill. The study site was Nipigon Bay on Lake Superior, approximately 100 km northeast of Thunder Bay, Ontario. The effluent of the pulp and paper mill was discharged into the western region of the bay at a rate of 9.4×10^7 ℓ/day (Domtar Pulp and Paper Co. personal communication). Enrichment of the bay by nutrients other than from the pulp and paper mill were minimal. The area of the bay bounded by Hughes Point, Ile La Grange and Burnt Island (Fig. 1) received the major influence of the effluent. The Nipigon River, at a maximum flow rate of 20,000 cfs (Ontario Hydro personal communication), entered the northeastern corner of the bay and water exited the bay mainly through the Nipigon Straits.

Nutrient enrichment of a water body resulted in an increase in the resident bacterial populations (Keeney et al. 1971) which reflected conditions that either stimulated the growth of bacteria or provided a more suitable environment for their survival. It was assumed that the influence of a pulp and paper mill waste would also be reflected by elevated bacterial populations in the receiving water. The extent of influence may be described by the spatial distributions of elevated bacterial populations and are represented by bacterial population contours. The decline of the influence within different sectors of the bay may be extrapolated from the distal decline of bacterial populations and is represented by regressions of bacterial numbers with distance.

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

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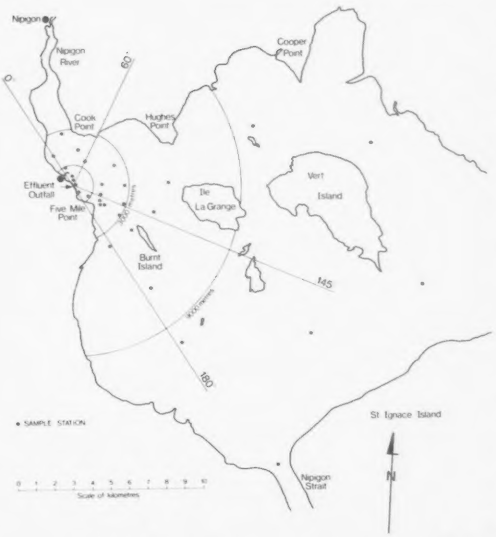

FIG. 1. Study site and sampling stations Nipigon Bay, Ont.

Materials and Methods

A zonal grid pattern was used in establishing the locations of sampling sites in the bay. Sampling stations (Fig. 1) were selected on a grid radiating through 0–180° into the bay and to a distance of 19 km from the effluent outfall. Water samples at 1 and 10 m depths were collected between July 16 and August 6, 1974 at weekly intervals from all stations within 10 km and once from stations beyond 10 km. A total of 88 water samples were taken, 76 from within 10 km and 12 from beyond 10 km of the outfall. A total of 36 1 m depth water samples, in conjunction with effluent plume movement studies (Fox 1975), were obtained on four individual days, at approximate weekly intervals, during the same time period. Sampling procedures and treatment of samples were as described by Rao et al. 1976.

Heterotrophic bacteria, total coliforms, fecal coliforms, organic sulfur reducers, sulfate reducers, and sulfur oxidizing bacteria were measured as described in Methods for Microbiological Analysis of Waters, Wastewaters and Sediments (Dutka 1974). All bacterial populations were expressed as $\log_{10}$ numbers per ml sample.

Mean heterotrophic populations in samples taken on different days, within 10 km of the effluent outfall, were significantly different (F-test, $P < 0.005$, 3 and 72 df). Since sampling programs for each day included all grid stations, the bacterial data from all days have been grouped. Mean heterotrophic populations in samples taken on different days, in conjunction with plume tracing experiments, were also significantly different (F-test, $P < 0.005$, 3 and 32 df) but sampling sites were within 2 km of the outfall and their bacterial numbers have also been grouped. Bacterial numbers in comparable samples taken at 1 and 10 m depths were not significantly different (t-test, $P > 0.05$, 34 df) and bacterial data from both depths were grouped.

The logarithmic means of populations of each bacterial type were calculated for each sampling station. Population ranges of 0.5 log units were arbitrarily selected and the bay was divided by contours inscribing sampling sites which contained similar bacterial populations.

Heterotrophic bacteria were dominant in all water samples and were selected as the test group for developing a method to demonstrate decline in bacterial numbers with distance (distal decline). Sampling stations within distance intervals of 500 m were grouped and the log-arithmetic mean and standard deviations of heterotrophic bacterial numbers were calculated. With random data, linear regressions of log numbers and linear distance and also log numbers and log distance were generated using program "Linear (01) CCIW Project ARD 071." The semi-log regression and the interpolated log–log regression were plotted on a semi-log axis and compared with the mean heterotrophic numbers from stations grouped into 500 m intervals.

Neither regressions of log numbers against linear distance nor log numbers against log distance, over 0–19 km, accurately described the decline in heterotrophic populations (Fig. 2). The most representative of the distal decline in heterotrophic bacterial numbers were linear regressions of log numbers against distance within the arbitrarily selected distance intervals of 0–3, 3–9, and 10–19 km. The latter regressions were used in describing the distal decline of all bacterial groups.

The bay was arbitrarily divided into angular intervals of 0–60° (North), 65–145° (East), and 145–180° (South) relative to an imaginary reference line parallel to the western shoreline. Each angular interval was subdivided into distance intervals of 0–3, 3–9, and 10–19 km (Fig. 1). Regressions of log bacterial numbers against distance were calculated within each of these sectors.

Results

Populations of all bacterial types were higher near the effluent outfall than in other regions of Nipigon Bay. Heterotrophic bacteria were the dominant group in all water samples with log numbers of 5 to 6/ml (10^5 to 10^6/ml) near the effluent outfall and 2.5 (300/ml) at the 19 km distance (Fig. 3a). Organic sulfur reducers were the next numerous (Fig. 4a) and were preponderant to sulfate reducers (Fig. 4b) and sulfur oxidizers (Fig. 4c). Populations of total and fecal coliforms (Fig. 3b and 3c) were the least numerous ranging from log numbers of 0 (1/ml) near the outfall to less than −2 (0.01/ml) at 10 km.

Within the first 3 km, all bacterial populations declined logarithmically with distance from the outfall (Fig. 5). The distal decline in numbers

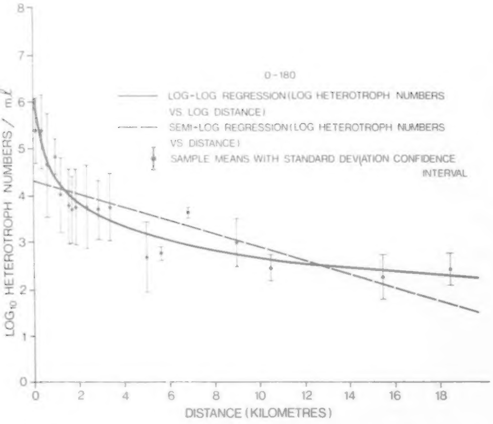

FIG. 2. Regressions of $\log_{10}$ heterotrophic numbers against distance and interpolated $\log_{10}$ heterotrophic numbers against $\log_{10}$ distance compared to the $\log_{10}$ mean heterotrophic bacterial numbers at 500 m distance intervals.

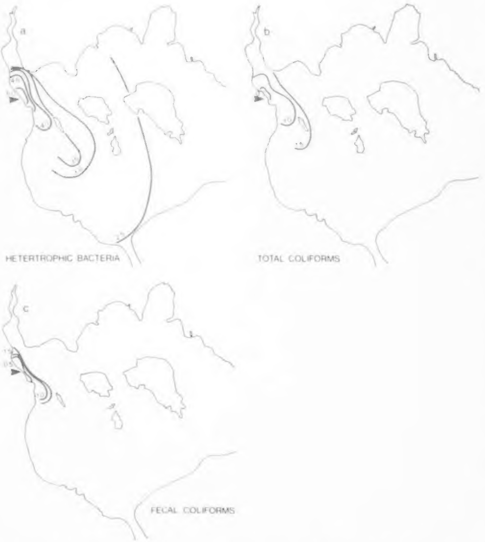

FIG. 3. Distributions of bacterial populations in Nipigon Bay (a) heterotrophic bacteria, (b) total coliforms, and (c) fecal coliforms. Contours were in 0.5 $\log_{10}$ intervals and inscribe waters containing similar bacterial populations.

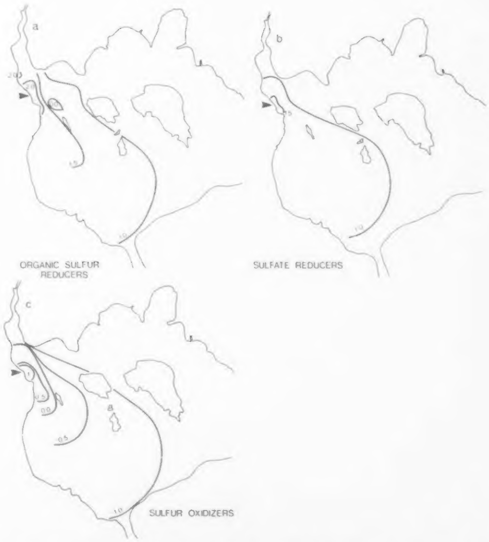

FIG. 4. Distributions of bacterial populations in Nipigon Bay (a) organic sulfur reducers, (b) sulfate reducers, and (c) sulfur oxidizers. Contours were in 0.5 $\log_{10}$ intervals and inscribe waters containing similar bacterial populations.

was variable with bacterial group and with all groups was less than the decline of the concentrations of sodium, a conservative variable indicating the dilution of the effluent (Rao et al. 1976). Thus, distal declines in bacterial numbers could not simply be explained by the dilution of non-growing populations and their decline may be a function of bacterial multiplication minus the dilution.

The decline in bacterial numbers over the first 3 km differed with direction from the effluent outfall. Populations of heterotrophic bacteria, total coliforms and fecal coliforms (Fig. 3), at numbers 1/10 of those at the outfall, persisted northward to the mouth of the Nipigon River and southward to Burnt Island, while similar population levels in the eastern direction were restricted to the first km. Within each of these bacterial groups, distal declines were similar in the northern (0–60°) and southern (145–180°) direction (Fig. 5). In the eastern direction (65–145°), distal declines were either more rapid (Fig. 5B and 5C) or bacterial numbers were lower throughout the interval (Fig. 5A).

In the 0–3 km interval, largest organic sulfur reducer populations were found in the northern (Fig. 4a), were at lower levels in the southern and declined most rapidly in the eastern direction (Fig. 5D). Sulfate reducing bacteria numbers were similar in the northern and southern directions and declined most rapidly in the eastern direction (Fig. 5F). Sulfur oxidizers were an exception with highest populations in the eastern direction.

Within the 3–9 km interval, elevated bacterial

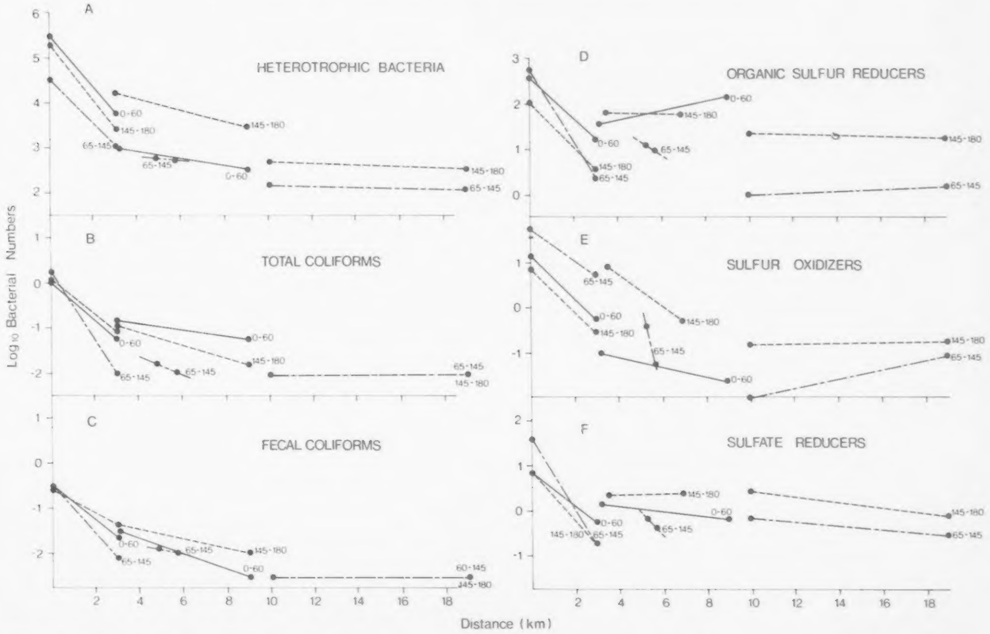

FIG. 5. Distal declines of bacterial numbers represented by regressions of $\log_{10}$ numbers against distance within intervals of 0–3, 3–9, and 10–19 km and in the northern, eastern, and southern direction. (A) heterotrophic bacteria, (B) total coliforms, (C) fecal coliforms, (D) organic sulfur reducers, (E) sulfur oxidizers, and (F) sulfate reducers.

populations were more sensitive than chemical concentrations as an indicator of an influence of the effluent on the receiving waters. Beyond 3 km of the effluent outfall, concentrations of sodium, sulfate, and total carbon were indistinguishable from baseline lake values (Rao et al. 1976). Bacterial populations in this interval, at numbers reduced from the preceding 3 km, were greater than baseline lake densities. Bacterial populations were also more stable as indicated by the generally reduced rate in distal decline of their numbers (Fig. 5).

The restriction of bacterial populations into the eastern direction was repeated in the 3–9 km interval. In this interval lowest levels of heterotrophic bacteria, total and fecal coliforms, organic sulfur reducers and sulfate reducers, and the most rapid distal decline of sulfur oxidizers were found in the eastern sector (Fig. 5). Similarly, population contours of all bacterial groups (Fig. 3 and 4) were restricted in the eastern direction.

At the mouth of the Nipigon River, 3 km north of the outfall, populations of heterotrophic bacteria (Fig. 3a and 5A) and sulfur oxidizers (Fig. 4c and 5E) were sharply reduced. In the river, populations of fecal coliforms and sulfate reducers were similar to their low levels in the eastern sector. Highest populations in the 3–9 km interval of total coliforms (Fig. 5B) and organic sulfur reducers (Fig. 5D) indicate a possible input of these bacteria from sources on the river.

The southern sector of the 3–9 km interval received the major effluent influence. Bacterial population contours (Fig. 3 and 4) extended to greater distances into the southern sector of the bay. Similarly, highest populations, within the 3–9 km interval, of heterotrophic bacteria, fecal coliforms, sulfur oxidizers and sulfate reducers (Fig. 5) were found in the southern sector.

The trend of elevated bacterial populations continued into the southern 10–19 km sector. Populations of heterotrophic bacteria, organic sulfur reducers, sulfur oxidizers, and sulfate reducers were larger than in the comparable eastern sector (Fig. 5). Heterotrophic bacteria and sulfur oxidizers were at reduced numbers from the preceding distance interval (3–9 km) while populations of organic sulfur reducers and sulfate reducers were similar, in southern sectors, over a distance of 3–19 km from the effluent outfall. Populations of heterotrophic bacteria and total coliforms in the eastern 10–19 km sector were similar to numbers in Lake Superior (Rao and Henderson 1974) and were assumed indicative of unaffected waters. Elevated numbers of heterotrophic and sulfur cycle bacteria in the southern sector of the bay demonstrated an influence of the effluent on the receiving waters to distances of 19 km from the outfall.

Discussion

The spatial extent of influence of a pulp and paper mill effluent on the receiving waters of Nipigon Bay was measured using bacterial populations as indicators. Bacteria were an alternative to chemical indicators such as conductivity, sodium, sulfur compounds, and organic carbon, traditionally used in describing mixing zones and zones of influence of an industrial waste. The influence measured by bacterial densities was the response to nutrient enrichment by organisms resident to the receiving waters. Since effluents of pulp and paper industries were known to enrich their receiving waters with organic carbon and sulfur compounds, bacteria utilizing these nutrients as substrates, heterotrophic and sulfur cycle bacteria, were indicators of the influence.

Bacterial population distributions were an effective indicator of the effluent's influence on the receiving waters of Nipigon Bay. In areas of the bay near the effluent outfall bacterial populations were maximal and declined with distance from the outfall, reflecting the expected distal decline in nutrients. In regions of the bay where concentrations of chemical indicators were indistinguishable from baseline lake values (Rao et al. 1976; Minns 1977), bacterial populations remained at numbers greater than those of unaffected waters, declined with distance, and continued to indicate a decline in influence. Influences could be detected by elevated bacterial populations to distances of 19 km, much farther than the 3 km distances detected by chemical indicators.

Distal declines in bacterial densities were most rapid over the first 3 km from the outfall indicating the most rapid reduction of influence in this region of the bay. Over the southern 3–9 km sector bacterial densities and distal declines in numbers were generally reduced indicating a lesser but more persistent influence than in the preceding 3 km. In the eastern 3–9 km sector, low levels of heterotrophic bacteria and rapid distal declines of sulfur cycle bacteria indicated a rapid disappearance of effluent influence. In the southern 10–19 km sector heterotrophic bacterial densities, marginally greater than in unaffected waters, indicated minimal organic carbon influences but a higher influence of sulfur compounds may have persisted into this sector as indicated by densities of sulfur cycle bacteria similar to those of the southern 3–9 km interval.

Bacterial population distributions in the bay indicated the effluent's penetration and influence in the bay was directional and was more obvious at distances greater than 3 km from the effluent outfall. Over the first 3 km influences penetrated equally in all but the eastern direction. A rapid decline in influence at the mouth of the Nipigon River, as indicated by declines in densities of heterotrophic, sulfur oxidizing and sulfate reducing bacteria, could be explained by the flushing of the area by the inflowing river. Rapid declines in influences in eastern sectors of the bay could have resulted from the predominant flow of water, in eastern sectors, toward the outfall (Polak and Palmer 1977). Most of the influence, as indicated by elevated numbers of heterotrophic and sulfur cycle bacteria, extended into the southern sectors of the bay.

A disadvantage encountered in the use of bacterial indicators was the variability between duplicate measurements as shown in the significant difference between station heterotrophic numbers on different days of the survey. A single survey was not sufficient and stations were sampled at least four times during the study period and all stations within 10 km of the outfall were sampled on the same day. Since many sampling stations at considerable distances into the bay were monitored, an extensive sampling program was required. In analysing the data, measurements at individual stations were grouped by pooling results from adjacent stations or generating regressions of bacterial numbers and distance within sectors of the bay. By pooling the data, the error encountered in measurements at one station was reduced.

The use of bacterial population distributions in analysing receiving waters of an industrial waste has proven valuable in detecting and describing variations in the influence of the effluent as well as delineating its spatial and directional distribution. It is recommended bacterial population distributions be used in evaluating the quality of receiving waters of industrial wastes.

DUTKA, B. J. 1974. Methods for microbiological analysis of waters, wastewaters and sediments. Inland Waters Directorate, Scientific Operations Division, Canada Centre for Inland Waters, Burlington, Ont.

FOX, M. E. 1975. Fate of selected organic compounds in the discharge of kraft mills in Lake Superior. Presented at the ISC Chemical Congress of North American Continent, Proceedings Symposium on Identification and Analysis of Organic Pollutants in Waters, Mexico City, Mexico.

KEENEY, D. R., R. A. HERBERT, AND A. J. HOLDING. 1971. Microbiological aspects of the pollution of fresh water with inorganic nutrients, p. 181–200. *In* G. Sykes and F. A. Skinner, Microbial aspects of pollution. Academic Press Inc., New York, N.Y.

MINNS, C. K. 1977. Analysis of a pulp and paper mill effluent plume. J. Fish. Res. Board. Can. 34. (This issue)

POLAK, J., AND M. D. PALMER. 1977. Concentration pattern of chemical constituents in a paper mill's effluent plume: dynamics and model. J. Fish. Res. Board Can. 34. (This issue)

RAO, S. S., AND J. P. HENDERSON. 1974. Summary report of microbiological baseline data on Lake Superior, 1973. Scientific Series No. 45, Inland Waters Directorate, Scientific Operations Division, Canada Centre for Inland Waters, Burlington, Ont.

RAO, S. S., D. A. ROKOSH, AND A. A. JURKOVIC. 1976. Influence of a point source pulp mill effluent discharge on the nearshore bacterial communities in Lake Superior, p. 397–408. *In* Proceedings of the Second Federal Conf. on Great Lakes. Great Lakes Basin Commission.

Organic Contaminant Residues in Fishes from Nipigon Bay, Lake Superior[1]

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KAISER, K. L. E. 1977. Organic contaminant residues in fishes from Nipigon Bay, Lake Superior. J. Fish. Res. Board Can. 34: 850–855.

Three species of fish, caught at various distances from a kraft pulp and paper mill effluent discharge in Nipigon Bay, were analyzed for organic contaminants. Fishes from all sites contained residues of polychlorinated biphenyls and DDE. Most samples were also contaminated with hexachlorobenzene and several samples contained phthalic acid esters.

From sampling sites close to the mill discharge, dehydroabietic acid was observed in one extract of each of the three fish species investigated. Two isomers of tetrachlorobenzene and one trichlorobenzene isomer were identified in a longnose sucker (*Catostomus catostomus*) extract from the vicinity of the mill outfall.

KAISER, K. L. E. 1977. Organic contaminant residues in fishes from Nipigon Bay, Lake Superior. J. Fish. Res. Board Can. 34: 850–855.

Nous avons dosé les substances organiques contaminantes dans trois espèces de poissons capturées à diverses distances de l'effluent d'un moulin de pâte et de papier kraft dans la baie Nipigon. Les poissons provenant de tous les sites contiennent des résidus de biphényls polychlorés et de DDE. La plupart des échantillons sont également contaminés par l'hexachlorobenzène, et plusieurs échantillons contiennent des esters d'acide phthalique.

Aux sites d'échantillonnage à proximité de l'émissaire du moulin, nous avons observé de l'acide déshydroabiétique dans un extrait de chacune des trois espèces de poissons étudiées. Nous avons identifié deux isomères de tétrachlorobenzène et un isomère de trichlorobenzène dans un extrait de meunier rouge (*Catostomus catostomus*) capturé dans le voisinage de l'émissaire du moulin.

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PULP and paper mills are among the largest industrial plants in northern Ontario and their effluents carry considerable amounts of cellulose fibers, lignin degradation products, terpenes, resin acids and process chemicals into adjacent waters. Nipigon Bay on Lake Superior experienced a dramatic decline of the walleye (*Stizostedion vitreum vitreum*) population in recent years. It has, therefore, been the site for a number of environmental studies evaluating the impact of local industries and towns on the fishery resource. In an extensive study by Ryder (1968), it was concluded, but without positive proof, that a kraft pulp and paper mill effluent in Red Rock, Nipigon Bay, was likely to be the reason for the change of the fish population. In addition, fishes from Nipigon Bay were increasingly found to have a strong foreign flavor which was associated with those kraft mill effluents (Chatterjee 1974). Flavor impairment of fish and acute toxicity evaluations of these pulp mill effluents were also studied by Whittle and Flood (1977).

The aim of the present investigation was the identification and analysis of organic compounds present at background levels in fish of Nipigon Bay that may directly or indirectly be introduced into the receiving waters from pulping processes and which may have deleterious biological effects. For this purpose, locally caught fishes were analyzed for such contaminants.

Materials and Methods

SAMPLE COLLECTION

Fishes were caught in gillnets of mesh size from 6.5 to 10.0 cm; for a detailed account on species and size distribution, see Kelso (1977). Four separate

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

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catches were obtained: (a) immediately off the kraft mill effluent outfall at Red Rock on July 17, 1974 (samples A); (b) approximately 300 m south of the kraft mill effluent outfall, on July 19, 1974 (samples B); (c) approximately 3.0 km east of the mill, off Hughes Point, on July 23, 1974 (samples C); and (d) off Vert Island, approximate location 48°54′N, 88°02′W on July 26, 1974 (samples D). The most abundant species and common to all sites were white sucker (*Catostomus commersoni*), longnose sucker (*Catostomus catostomus*), and yellow perch (*Perca flavescens*) and were selected for this study.

SAMPLE PREPARATION

All tissue samples were ground and extracted within a few hours after fish were netted. Whole fish or selected tissues (Table 1), were placed in beakers and were macerated with a Polytron® high speed blender, model P.T. 45/OD. The samples or subsamples thereof, weighing 20 to 40 g, were then mixed with anhydrous sodium sulfate (Analar®) at a ratio of 2.5 to 5.0 times the tissue weight to nearly dry consistency and were placed in glass columns of 2 cm diameter and length of 40 cm, fitted with fritted glass and Teflon® stopcocks. Each sample was extracted with approximately 150 ml hexane:ether (2:1). The eluent was collected and the solvent stripped under vacuum at approximately 40°C. The resulting fish oils were stored in glass vials at room temperature until further workup.

For the determination of DOE and polychlorinated biphenyls, the oils were subjected to routine Florisil® cleanup procedures and were quantitatively analyzed by routine gas chromatographic methods (Chau and Sampson 1975).

For a more detailed investigation of the oils, 1 ml aliquots were dissolved in diethyl ether and were methylated with diazomethane solutions in diethyl ether. Subsequently, the ether was stripped at 40°C and the samples were redissolved in hexane. Such hexane solutions were placed on neutral alumina ('Baker Analyzed' Reagent) in glass columns of 2 cm diameter and 10 cm length in hexane. These columns were eluted, first with 150 ml hexane, then with an equal volume of diethyl ether, yielding hexane and ether extracts, respectively. Both types of extracts were concentrated under vacuum at 40°C, the ether fraction after addition of 50 ml hexane. Hexane solutions of both the hexane and ether extracts were analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS).

SAMPLE ANALYSIS

Experimental conditions of GC and GC–MS analyses were closely matched. For the GC, a Tracor MT 220 gas chromatograph with 1.8 m, 4 mm glass column with 3% OV-1 on Chromosorb W-HP was employed. For a simultaneous observation of both flame ionization detector (FID) and electron capture detector (ECD) responses, the gas chromatograph was fitted with a one to one splitter device between the column and the detectors. The column temperature was programmed at either 12 or 20°C per minute with an inlet temperature of 250°C and detector temperature of 250°C (FID) and 300°C (ECD), respectively. Prepurified nitrogen at a flow rate of 80 ml/min and a head pressure of 2.6 kg/cm^2 as carrier gas was used in combination with an argon: methane mixture (9:1) at a flow rate of 18 ml/min and a head pressure of 2.1 kg/cm^2 as purge gas for the ECD.

The GC–MS investigations were performed with a Finnigan 1015 instrument with computerized data acquisition. The GC conditions were closely matched with those above. Transfer line and separator temperatures were kept at 200°C; the ion source temperature at 50°C. The electron impact energy was 70 eV; the integration times varied from 1 to 30 ms per atomic mass unit.

Results and Discussion

POLYCHLORINATED BIPHENYLS AND DDE

Sediment samples from Lake Superior indicated a large source of polychlorinated biphenyls (PCBs) at Marathon (Anon. 1976). Similarly, whitefish (*Coregonus clupeaformis*) netted near Marathon showed PCB residues much above those from other nearshore areas of Lake Superior (Ontario Ministry of the Environment 1975). In contrast, the effluents of industrial plants at Sault Ste-Marie had no detectable concentrations of PCBs (Ontario Ministry of the Environment 1973). It appeared therefore of interest to investigate the Nipigon Bay area to ascertain whether or not elevated levels of PCBs were present in fish from this area.

All samples and tissues analyzed contained polychlorinated biphenyl (PCB) and *p,p′*-dichlorophenyl-1, 1-dichloroethylene (DDE). PCB residues are found as ubiquitous contaminants of aquatic life (Peakall 1975) and DDE is, under reducing conditions, the most persistent metabolite of the once widely used insecticide DDT. Usually DDE represents between 60 and 90% of the total DDT (DDT plus all DDT metabolites). Table 1 lists the samples analyzed and the residue levels observed. The range of PCB residues in those viscera samples which were analyzed quantitatively was from 0.04 to 0.80 μg/g on a wet weight basis, while in the same samples DDE residues ranged from 0.025 to 0.25 μg/g. White sucker had the least contamination with mean residues of 0.09 μg/g PCB and 0.04 μg/g DDE, respectively, in their viscera. The corresponding residue means for longnose sucker were 0.22 μg/g PCB and 0.14 μg/g DDE; those for yellow perch were 0.40 μg/g PCB and 0.15 μg/g DDE, respectively.

The observed residue level of PCBs and DDE in fishes from Nipigon Bay were of the same magnitude as those reported for Lake Superior

TABLE 1. Species, length, selected tissue, source area, PCB and DDE residues, and PCB:DDE residue ratios of investigated fish samples from Nipigon Bay.

Species	Length (*cm*)	Tissue	Source area	PCB (μg/g)	DDE (μg/g)	PCB:DDE ratio
White sucker	47	viscera	B	0.08	0.035	2.3
	48	viscera	C	0.04	0.025	1.6
	48	skin	C	0.016	0.011	1.5
	47.5	viscera	D	0.15	0.06	2.5
		viscera	mean	0.09	0.04	2.1
Longnose sucker	40	viscera	A	0.19	0.17	1.1
	33	viscera	C	0.15	0.05	3.0
	34	viscera	D	0.32	0.20	1.6
		viscera	mean	0.22	0.14	1.9
Yellow perch	23.5	whole	A	0.13	0.07	1.9
	31	viscera	A	0.18	0.09	2.0
	29	viscera	C	0.80	0.25	3.2
		skin		0.10	0.05	2.0
	19[a]	viscera	C	0.09	0.03	3.0
	30	viscera	D	0.51	0.22	2.3
		viscera	mean	0.40	0.15	2.6

[a] Combined viscera of three specimens of equal lengths.

fishes (Ontario Ministry of the Environment 1975). The residue means of both PCBs and DDE were higher in yellow perch than in longnose sucker and white sucker, the latter having the lowest mean values of the three species. This may be due, in part, to differences in their body chemistry and location in the food chain. Longnose sucker appeared to have a higher content of fat than white sucker. Large yellow perch are predators and are therefore likely to have higher dietary intakes of PCBs and DDE than the bottom feeding suckers. The PCB:DDE ratios given in Table 1 varied in all samples from 1.1 to 3.2 with similarly large fluctuations in each fish species. This may be due, in part, to the relatively high error limits for these determinations near the present quantification limit of 0.01 μg/g PCB in fish tissues. In most samples, the observed GC pattern of the PCBs resembled that of Aroclor® 1242 and 1254. Some samples, however, showed GC patterns with the later eluting PCB peaks enriched relative to earlier peaks.

CHLOROBENZENES

Hexane and diethyl ether fractions of the methylated fish oils were investigated by GC with the simultaneous monitoring of the column effluent with ECD and FID. This technique allows a good distinction between closely eluting compounds, particularly in the frequent case of their specific signal strengths being different with the two detectors.

The ether fractions of the methylated fish oils did not show any significant FID variations between the samples of the same species and from different sites. The FID gas chromatograms of such fractions are dominated by lipid materials. The major components were identified as the methyl esters of oleic, palmitic and stearic acid by mass spectra comparison only. The mass spectra of several other eluting compounds appeared to be esters of other natural fatty acids, which were not investigated further.

The hexane fractions of the methylated samples were of interest with respect to their content of persistent compounds. Figure 1 gives both the FID and ECD gas chromatographic traces of the hexane fraction of a longnose sucker (*Catostomus catostomus*) caught close to the pulp mill effluent outfall. As evident from Fig. 1, each detector responds to a number of compounds, some of which are overlapping. ECD and FID chromatograms are distinctly different, emphasizing the different specific detector sensitivities to the various compounds.

In detail, the ECD trace in Fig. 1 shows a large group of signals at the high temperature end of the chromatogram. These compounds are polychlorinated biphenyls in a pattern resembling Aroclor® 1254. In addition, the chromatogram shows three other distinct GC peaks of compounds

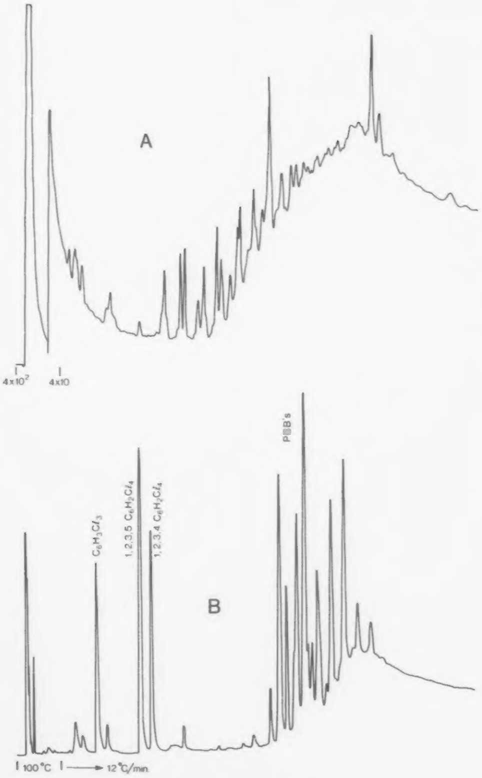

FIG. 1. Flame ionization detector (A) and simultaneous electron capture detector (B) gas chromatograms of the hexane extract of a longnose sucker (*Catostomus catostomus*) from site (A), Nipigon Bay.

eluting at much lower temperatures. Two of these compounds were identified as tetrachlorobenzene isomers. While hexachlorobenzene was observed in comparable quantities in many samples from all areas, the tetrachlorobenzenes appeared to be peculiar to this specimen. The identity of this benzene compound, hitherto unobserved in environmental samples, was confirmed by GC in comparison with an authentic sample. The mass spectrum of this compound shows a base peak of m/e 216 atomic mass units (amu) with a chlorine isotope cluster typical for a compound with four chlorine atoms per molecule and with a molecular ion of M^+ of 214 amu. A quite similar mass spectrometric fragmentation is observed for the gas chromatographic peak immediately following. It can thus be assumed to be one of the other two possible tetrachlorobenzene isomers. Based on the longer GC retention times compared with the 1,2,3,5-tetrachlorobenzene, this compound is tentatively identified as 1,2,3,4-tetrachlorobenzene. This is also consistent with the boiling points of both compounds, which are 246 and 254°C, respectively.

The mass spectrum of one compound eluting at an even lower temperature than the tetrachlorobenzene and its isotope cluster in combination with the base peak M^+ of 180 amu allows the identification of this compound as one of three possible trichlorobenzene isomers. No attempts were made to determine its exact structure and no quantitative determination of the chlorobenzenes was undertaken.

PHTHALIC ACID ESTERS

A number of hexane fractions of samples from all areas also contained one or more phthalic acid esters. Compounds identified by comparison of mass spectra were two dioctylphthalates and dibutylphthalate. Although phthalates are known as lignin degradation products (Brink et al. 1966), the presence of such compounds in fishes from an area remote to the pulp mill appears surprising. As shown by Kelso (1977), movement of fish is quite pronounced and the life history of the collected specimens is unknown. All samples were handled with precautions but a secondary contamination by phthalates after the fish were netted cannot entirely be excluded. Particularly in view of the rapid biodegradation of phthalates in fish (Stalling et al. 1973), the observation of phthalates in samples from the Vert Island area appears questionable. However, it should be pointed out that several phthalic esters were consistently observed in water samples from Nipigon River and Nipigon Bay, also at locations near Vert Island (Brownlee and Strachan 1977; Fox 1977). For an explanation of these findings, both a source within and outside the pulp mill is indicated.

RESIN ACIDS

Of special interest to this investigation are persistent and toxic organic compounds which are released from coniferous wood with or without chemical modification during the pulping process. Resin acids were identified among these toxic constituents of kraft pulp mill effluents (Leach and Thakore 1973; Rogers 1973; Rogers et al. 1975). In concurrent field studies by Brownlee and Strachan (1977) and by Fox (1977) the persistence of resin acids, and dehydroabietic acid in particular, in these receiving waters was shown. Laboratory investigations by Mahood and Rogers (1975) and by Fox and Kaiser (unpublished data) established the uptake of this resin acid by sockeye salmon (*Oncorhynchus nerka*) and by rainbow trout (*Salmo gairdneri*) from water.

As pointed out by Mahood and Rogers (1975), the analysis of fish for resin acids is complicated by the presence of large amounts of fatty acids and other lipids in fish extracts. These interfere with the gas chromatographic analysis of the resin acids, and a cleanup by chemical or physical means prior to the GC analysis is necessary. We observed a partial separation of dehydroabietic acid (DHA) from the bulk of lipids by column chromatography of methylated fish extracts on neutral alumina. The methyl ester of DHA elutes in part together with other materials in the hexane fraction (*vide infra*) while the major portion of lipids is retained on the column.

Although the presence of DHA in such hexane extracts is still difficult to ascertain by GC only, a computerized GCMS can easily depict its presence due to its characteristic mass spectrum. Figure 2A shows the computer-reconstructed gas chromatogram of the hexane extract of the skin tissue of a white sucker (*Catostomus commersoni*) captured approximately 3 km from the pulp mill discharge (area C). The mass spectrum of spectrum number 137 (Fig. 2B) of this chromatogram clearly identifies the observed GC peak as the methyl ester of DHA. Less evident, the same compound was observed in the hexane fractions of the viscera of a yellow perch (*Perca flavescens*) and in a longnose sucker (*Catostomus catostomus*), both taken from the site (A), close to the kraft mill discharge. No attempts were made to quantitatively determine the DHA in these samples.

In view of the observation of DHA in the above samples only, and its absence in extracts of fish from the remote site (D), the presence of the contaminant in fish appears to be related to the kraft mill effluent, which contains large amounts of this and other resin acids (Fox 1977). Undoubtedly, DHA is to be found at small concentrations in most natural waters where coniferous wood is present. Such concentrations however, appear to be insufficient to result in measurable residues in fish inhabiting such waters. In addition, the uptake of resin acids from water by fish, which was demonstrated by Mahood and Rogers (1975) and by Fox and Kaiser (unpublished data), may be a reversible process. This hypothesis, however, must await experimental proof.

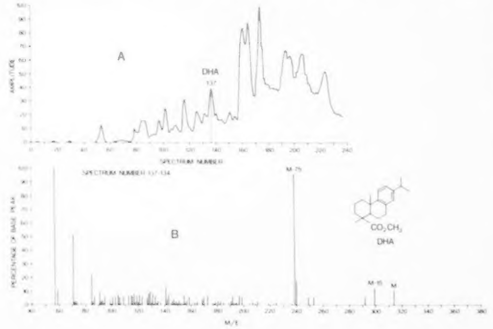

FIG. 2. Computer reconstructed gas chromatogram (A) and mass spectrum of spectrum number 137 (B), identified as dehydroabietic acid methyl ester, of the hexane extract of a white sucker (*Catostomus commersoni*), from site C, Nipigon Bay.

The finding of dehydroabietic acid in fish from the vicinity of the pulp mill discharge is likely to be associated with contaminants in the effluent itself. Chlorobenzenes other than hexachlorobenzene, have hitherto not been reported in such samples. Their presence could be explained as a result of chlorine bleaching processes which are known to form chloro compounds, such as dichloro- and trichloro-veratrole (Brownlee and Strachan 1977), or as metabolites of such chloro compounds.

Dehydroabietic acid and other resin acid derivatives are widely found in the Nipigon Bay area (Brownlee et al. 1977), and it has been shown that kraft pulp and paper mill effluents are their major source. The observation of such contaminants in fishes from Nipigon Bay is complimentary to their presence in fish experimentally exposed to pulp mill effluents (Fox and Kaiser unpublished data).

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ANON. 1976. Background to the regulation of polychlorinated biphenyls (PCB) in Canada. A report of the Task Force on PCB, April 1, 1976, to the Environmental Contaminants Committee of Environment Canada and Health and Welfare Canada. Tech. Rep. 76-1: 169 p.

BRINK, D. L., J. G. BICHO, AND M. M. MERRIMAN. 1966. Oxidative degradation of wood. III. A comparison of products by nitrobenzene, molecular oxygen, and nitric acid oxidation, p. 177–204. *In* Lignin structure and reactions. Advan. Chem. Ser. 59.

BROWNLEE, B., M. E. FOX, W. M. J. STRACHAN, AND S. R. JOSHI. 1977. Distribution of dehydroabietic acid in sediments adjacent to a kraft pulp and paper mill. J. Fish. Res. Board Can. 34. (This issue)

BROWNLEE, B., AND W. M. J. STRACHAN. 1977. Distribution of some organic compounds in the receiving waters of a kraft pulp and paper mill. J. Fish. Res. Board Can. 34. (This issue)

CHATTERJEE, R. M. 1974. Fish tainting in the upper Great Lakes. Ont. Minist. Environ. Water Resour. Branch Rep. 31 p.

CHAU, A. S. Y., AND R. SAMPSON. 1975. Electron capture gas chromatographic methodology for the quantification of polychlorinated biphenyls; survey and compromise. Environ. Lett. 8: 89–101.

FOX, M. E. 1977. Persistence of dissolved organic compounds in kraft pulp and paper mill effluent plumes. J. Fish. Res. Board Can. 34. (This issue)

KELSO, J. R. M. 1977. Density, distribution, and movement of Nipigon Bay fishes in relation to a pulp and paper mill effluent. J. Fish. Res. Board Can. 34. (This issue)

LEACH, J. M., AND A. N. THAKORE. 1973. Identification of the constituents of kraft pulping effluent that are toxic to juvenile coho salmon (*Oncorhynchus kisutch*). J. Fish. Res. Board Can. 30: 479–484.

MAHOOD, H. W., AND I. H. ROGERS. 1975. Separation of resin acids from fatty acids in relation to environmental studies. J. Chromatogr. 109: 281–286.

ONTARIO MINISTRY OF THE ENVIRONMENT. 1973. Working group C on land source inputs. Int. Joint Comm. Upper Lakes Ref. Group. Rep. C-201.

ONTARIO MINISTRY OF THE ENVIRONMENT. 1975. Working group D. Lake Superior assessment of nearshore fisheries. Int. Joint Comm. Upper Lakes Ref. Group. Rep. D-20.

PEAKALL, D. B. 1975. Polychlorinated biphenyls and their environmental effects. CRC Crit. Rev. Environ. Control. p. 469–508.

ROGERS, I. H. 1973. Isolation and chemical identification of toxic components of kraft mill wastes. Pulp Pap. Mag. Can. 74: 303–308.

ROGERS, I. H., ET AL. 1975. Fish toxicants in kraft effluents. Tappi 58: 136–140.

RYDER, R. A. 1968. Dynamics and exploitation of mature walleyes (*Stizostedion vitreum*) in the Nipigon Bay region of Lake Superior. J. Fish. Res. Board Can. 25: 1347–1376.

STALLING, D. L., J. W. HOGAN, AND J. L. JOHNSON. 1973. Phthalate ester residues. Their metabolism and analysis in fish. Environ. Health Perspect. 4: 519–173.

WHITTLE, D. M., AND K. W. FLOOD. 1977. Assessment of the acute toxicity, growth impairment, and flesh tainting potential of a bleached kraft mill effluent on rainbow trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 34. (This issue)

Effect of a Pulp and Paper Mill Effluent on the Productivity of Periphyton and Phytoplankton[1]

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MOORE, J. E., AND R. J. LOVE. 1977. Effect of a pulp and paper mill effluent on the productivity of periphyton and phytoplankton. J. Fish. Res. Board Can. 34: 856–862.

The short-term effect of a kraft mill effluent on the productivity of periphyton and phytoplankton in Nipigon Bay was examined. Addition of raw effluent at concentrations of 10^{-2} and higher consistently reduced photosynthesis of both periphyton and phytoplankton. Significant reductions were occasionally observed at effluent concentrations as low as 10^{-4}. At high effluent concentrations pH change produced a major portion of the depression. Laboratory experiments with four compounds identified from the effluent showed dehydroabietic acid to be slightly toxic.

MOORE, J. E., AND R. J. LOVE. 1977. Effect of a pulp and paper mill effluent on the productivity of periphyton and phytoplankton. J. Fish. Res. Board Can. 34: 856–862.

Les auteurs ont étudié l'effet à court terme de l'effluent d'une papeterie kraft sur la productivité du périphyton et du phytoplancton dans la baie Nipigon. L'addition d'effluent non traité à des concentrations de 10^{-2} et plus entraîne toujours une diminution de la photosynthèse du périphyton aussi bien que du phytoplancton. On a observé occasionnellement des diminutions significatives à des concentrations d'effluent aussi faibles que 10^{-4}. A de hautes concentrations d'effluent, le changement de pH est responsable de la majeure partie de la diminution. Des expériences de laboratoire avec quatre composés identifiés dans l'effluent démontrent que l'acide déshydroabiétique est légèrement toxique.

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IF an effect of waste discharged from a pulp mill is to alter the productivity of algae in the receiving waters, then that effect alone may have far-reaching consequences for the ecosystem as a whole. Studies of the impact of pulp mill effluents on aquatic biota have, however, been largely restricted to fish with almost no attention paid to effects on algae. Rainville et al. (1975) have examined the toxicity of several kraft mill discharges to the marine alga *Coccochloris elebans* in culture. Eloranta and Eloranta (1974) studied the effects of sulphite mill wastes on the growth of *Ankistrodesmus falcatus* in culture and looked at phytoplankton biomass and primary production in the receiving water. Stockner et al. (1975) have examined the effects of kraft mill effluents on marine phytoplankters. At the time of this study there were no published investigations of the response to kraft effluents of natural populations of freshwater periphyton and phytoplankton. The purpose of this study, therefore, was to determine the effect of the effluent from the kraft mill at Red Rock on the productivity of these organisms occurring in Nipigon Bay, Lake Superior.

Methods

PERIPHYTON

Periphyton were allowed to colonize 5 × 20 cm strips of cellulose acetate mounted on a moveable steel frame which could be raised to the surface for sampling. The frames with their acetate strips were situated at a depth of 2 m at two locations, one near the discharge canal and the other at a reference site 1.5 km north of the pulp mill. While it may be argued that this approach to periphyton sampling does not duplicate natural conditions (Tippet 1970),

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

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the use of acetate strips reduces the problems of sampling, experimentation, and radioassay to extreme simplicity.

For each of the five experiments conducted, a surface water sample was collected 0.5 km north of the mill and filtered through a GF/C glass fiber filter to remove phyto- and zooplankton. This filtered water served as control water and was used to dilute an effluent sample collected in the mill discharge channel at the final foam barrier to yield five effluent concentrations of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, and 0. Thirty 100-ml glass reagent bottles were filled with these prepared dilutions, six for each of the five treatments. These were taken to the reference site where a frame was raised and strips of acetate cut into smaller strips (approximately 2 cm^2), one such strip being allowed to drop into each bottle as it was cut. The bottles were then returned to the laboratory where each was inoculated with 100 μl of a $Na_2{}^{14}CO_3$ solution (20 $\mu c \cdot ml^{-1}$) and tightly stoppered. Four of the six bottles for each dilution were then exposed to light and two placed in the dark, giving duplicate light bottles and one dark bottle for an exposure period of 2 h and the same for a period of 4 h.

The apparatus employed for exposure consisted of a large rectangular plexiglas tank illuminated from one side by a vertical bank of 16 1-m high output daylight fluorescent lamps. The tank was filled with water and kept at constant temperature by a Neslab HX-50 heat pump. Light intensity was approximately 20 Klux and the temperature was set close to that of the control water sample at the time of collection. Within the tank was a large plexiglas wheel rotating in the plane of the lamps to which wheel the bottles were affixed.

After exposure, the contents of the bottles were vacuum-filtered at 120 mm Hg through 0.45 μm Sartorius cellulose acetate membrane filters, followed by washing with 10 ml filtered lake water. Filtering was necessary to recover any organisms which may have become dislodged from the acetate strip during incubation. After filtering, the area of the strips was measured, and filters and strips were stored in open plastic scintillation vials. Filters and strips were subsequently fumed for 10 min over HCl to remove any ^{14}C precipitated as monocarbonates (Wetzel 1965).

The activity of these samples was determined using a Nuclear–Chicago Unilux II scintillation counter employing the channels-ratio quench correction method. Each vial was filled with 15 ml of a dioxane-based flour (Bray 1960), shaken 20 min to dissolve strip and filter, and counted to 10,000 counts or 20 min. The results in DPM were used along with values for total dissolved inorganic carbon and the area of the strips to compute carbon uptake rates in mg C m^{-2} h^{-1}.

In addition to the five experiments performed as above, another was conducted in which reference site organisms were used in one series of effluent dilutions and a parallel series was set up using organisms from the discharge site. Other details of the experiment were the same as above.

PHYTOPLANKTON

Control water samples were collected at the same location as for periphyton and used with no further treatment to prepare effluent dilutions. One series was prepared on each of 3 days with concentrations of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, and 0, while on two other occasions the concentrations employed were 10^{-1}, 5×10^{-2}, and 0. Four light bottles and two dark bottles were prepared for each concentration, inoculated with ^{14}C, and exposed in the constant temperature light box for two exposure periods of 2.1–2.3 h (exposure I) and 4.4–5.5 h (exposure II). After exposure, samples were filtered through 0.45 μm Sartarius cellulose nitrate membrane filters and filters stored as above. Prior to counting, the vials were filled with 15 ml PCS fluor (Amersham-Searle Corp) and shaken 10 min to dissolve the filter. Counting results in DPM were used to compute carbon uptake rates in mg C $m^{-3} \cdot h^{-1}$ which were subsequently corrected for the volume of effluent introduced. Other details of the experiments were the same as given previously for periphyton.

In addition to the experiments above, another was performed to assess the role of effluent pH in contributing to the effluent's effect on photosynthesis. For this purpose, one series was prepared exactly as before, using effluent concentrations of 10^{-1}, 10^{-2}, 10^{-3}, and 0 and the pH of each measured. In addition, a second series at 10^{-2} and 10^{-1} was made up using effluent adjusted to control sample pH with concentrated H_2SO_4 as well as a third series consisting of control water with pH adjusted with 2N NaOH to that of the 10^{-1} and 10^{-2} raw effluent treatments.

LABORATORY EXPERIMENTS

Subsequent to the field studies, an attempt was made to determine the effect of a representative of each of four major classes of organics identified in the mill effluent (Fox 1977). The compounds selected were dehydroabietic acid, oleic acid, guaiacol and α-terpineol. Two experiments were conducted, one examining the effect of each compound at various concentrations and the other comparing the effect of these materials at high concentrations to two concentrations of a sample of frozen mill effluent.

The test organism, *Cryptomonas erosa*, was cultured in W.C. medium (Guillard and Lorenzen 1972) at pH 7.5, 15°C, and an 8 h light–16 h dark regime. In the first experiment the compounds were tested at 0, 0.5, 5, 50, and 500 $\mu g/\ell$. In the second experiment each substance was run at 0 and 500 $\mu g/\ell$ and the frozen effluent tested at 10^{-1} and 10^{-2}. The experimental design was such that for both experiments three replicate samples were prepared for each compound (including effluent) at each concentration. The chemicals added were made up in acetone to concentrations such that the addition of 100 $\mu\ell$ to a 100 ml incubation bottle would yield the desired final concentration. Three acetone controls were included in the first experiment.

Incubation bottles were filled from stock culture diluted to 6×10^3 cells$\cdot ml^{-1}$ and the chemicals

TABLE 1. Mean carbon uptake for A) periphyton and B) phytoplankton with various effluent concentration.

A) Date	Exposure	Concentration				
		0	10^{-4}	10^{-3}	10^{-2}	10^{-1}
29/7/74	2 h	1.95	1.35	1.45	0.90	−0.10
“	4 h	1.70	1.90	1.10	0.75	0.10
31/7/74	2 h	4.28	4.01	3.39	2.60	0.79
“	4 h	3.47	3.25	3.23	2.48	0.57
2/8/74	2 h	4.29	3.58	3.42	2.32	0.48
“	4 h	4.53	3.90	3.37	2.23	1.01
5/8/74	2 h	2.29	2.25	2.17	1.07	0.11
“	4 h	2.08	1.56	1.09	0.43	0.23
6/8/74	2 h	7.00	6.48	5.62	3.45	0.58
“	4 h	6.21	4.95	4.34	3.72	0.24

B) Date	Exposure	Concentration				
		0	10^{-4}	10^{-3}	10^{-2}	10^{-1}
19/7/74	I	12.50	7.90	6.79	7.71	4.07
	II	9.10	7.50	7.13	6.33	3.90
20/7/74	I	6.40	5.61	5.87	4.98	−0.26
	II	6.53	5.84	5.95	4.83	0.18
26/7/74	I	7.45	7.67	7.79	6.84	1.76
	II	6.32	6.44	6.68	5.89	1.78
30/7/74	I	3.69	3.91	3.49	2.76	0.49

Date	Exposure	Concentration				
		0	10^{-2}	2×10^{-2}	5×10^{-2}	10^{-1}
22/7/74	I	6.28	5.31	4.57	3.04	1.20
	II	6.01	5.08	4.28	3.03	1.49
24/7/74	I	7.57	6.59	6.31	4.28	1.72
	II	6.92	5.96	5.22	3.81	2.55

pipetted directly into the bottles. Other details of the experiments are the same as previously given for the field studies with phytoplankton.

Results

PERIPHYTON

Carbon uptake rates (Table 1) obtained with the control site organisms varied widely from day to day, ranging from 1.7 to 7.0 mg $C \cdot m^{-2} \cdot h^{-1}$. Carbon uptake rates at the different effluent concentrations also varied considerably (Fig. 1), but in general, the effluent reduced photosynthesis, the magnitude of inhibition increasing with increasing effluent concentration. For a more detailed analysis of the data, a two-way analysis of variance (concentration vs. time) was performed on each of the five experiments along with the computation of least significant differences (Table 2). The resulting large *F* values for the concentration mean square confirmed the inhibitory effect of the effluent, concentration accounting for 84–92% of the total sum of squares. Significance of individual treatment effects in each experiment was examined by paired comparisons employing the computed least significant differences. In all cases, the effect was significant at concentrations of 10^{-1} and 10^{-2}, and on the last two dates photosynthesis was also significantly reduced at 10^{-3} and 10^{-4}. On no occasion was significant stimulation of photosynthesis observed.

A tendency was observed (Table 1) for rates determined over 4 h to be less than the corresponding 2-h rates for all treatments, including controls. In the case of the last two experiments, the mean square attributable to this effect was significant (Table 2). In one case there was significant interaction between the effect of effluent concentration and the exposure times employed.

The experiment comparing the performance of discharge site organisms with those from the reference site (Fig. 2) resulted in an interesting contrast. Growth at the discharge site was much heavier so that rates of carbon uptake determined with strips from this site were greater than those obtained with strips from the reference site. However, the inhibitory effect of the effluent was also greater for the discharge site organisms in

TABLE 2. Two-way analysis of variance for: A) periphyton and B) phytoplankton incubated for two exposure times in five effluent concentrations. * significant ($P < 0.05$), ** significant ($P < 0.01$), † least significant difference ($P < 0.05$).)

			SS		*F*			
	Date	*N*	Total	Error	Conc. (4, 10 df)	Time (1, 10 df)	Inter (4, 10 df)	LSD†
A)								
	29/7/74	20	10.098	1.080	19.602**	0.000	1.273	0.73
	31/7/74	20	30.166	2.091	31.976**	4.118	0.560	1.02
	2/8/74	20	35.989	2.387	34.729**	0.748	0.283	1.09
	5/8/74	20	12.158	0.281	97.333**	15.712**	4.515*	0.37
	6/8/74	20	101.410	2.922	80.158**	9.193*	1.799	1.20
B)								
	19/7/74	20	113.147	6.042	38.767**	8.128*	3.525*	1.73
	20/7/74	20	112.903	0.376	746.221**	2.872	1.239	0.43
	22/7/74	20	58.132	1.096	129.548**	0.457	0.557	0.74
	24/7/74	20	68.883	0.717	227.455**	11.269**	7.406**	0.60
	26/7/74	20	90.857	0.422	506.569**	91.754**	6.242**	0.46

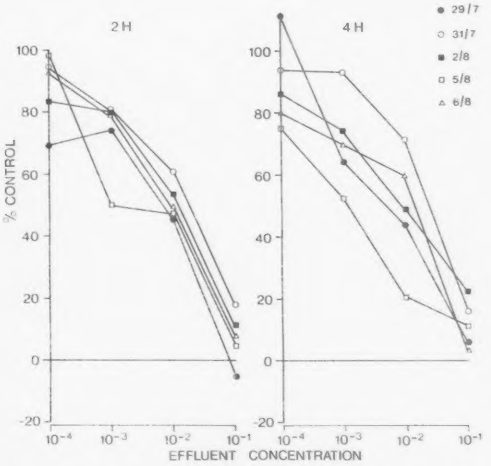

FIG. 1. Periphyton carbon uptake (% of control) at four effluent concentrations.

spite of the fact that they were growing at least some of the time in water contaminated by the effluent plume.

PHYTOPLANKTON

The photosynthetic rates obtained with phytoplankton were analyzed in a manner identical to that employed for the periphyton. Again, rates were highly variable from day to day (Table 1), control values ranging from 3.7 to 12.5 mg $C \cdot m^{-3} \cdot h^{-1}$. As with periphyton, the short-term effect of the effluent (Fig. 3) was to reduce photosynthesis, the effect increasing with increasing concentration. Results of the analysis of variance (Table 2) were similar to those for periphyton, concentration accounting for 84–99% of the total sum of squares. Effluent treatment effects were significant at 10^{-1} on all occasions and on all but one occasion at 10^{-2}. Significant effects were also observed at 10^{-3} and 10^{-4} in the first two experiments. When effects expressed as per cent of control are averaged for

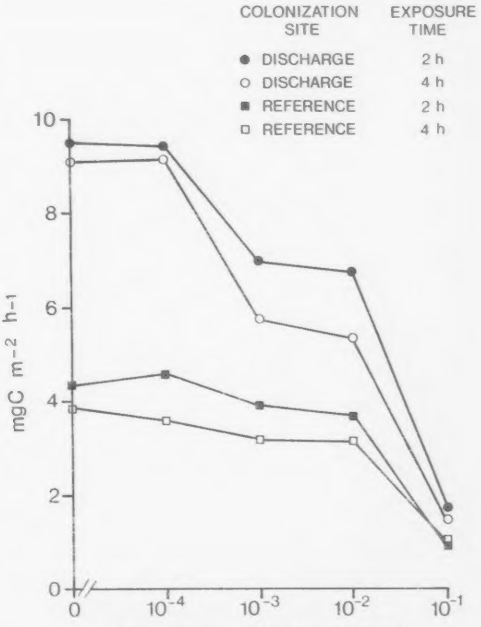

FIG. 2. Carbon uptake (mg $C \cdot m^{-2} \cdot h^{-1}$) at four effluent concentrations, obtained with periphyton from discharge and reference sites.

TABLE 3. Carbon uptake by phytoplankton exposed to effluent at various concentrations and pHs on August 1, 1974. Exposure time was 2.82 h. Raw effluent pH was 9.86.

	Control	Raw effluent			pH adjusted effluent		pH adjusted control	
effluent concentration	0	10^{-3}	10^{-2}	10^{-1}	10^{-2}	10^{-1}	0	0
final pH	7.97	—	8.10	8.98	7.97	7.97	8.06	8.99
carbon uptake	4.2	3.7	2.7	0.4	3.2	0.9	3.7	1.3
($mg\ C \cdot m^{-3} \cdot h^{-1}$)	4.6	3.7	2.6	0.3	2.8	0.9	3.9	1.3
	4.0	3.5	2.8	0.4	2.9	0.9	4.1	1.3
mean	4.3	3.6	2.7	0.4	3.0	0.9	3.9	1.3
% of control	100	85*	64*	9*	69*	21*	92	30*

One-way analysis of variance (log transformed data):

Source	df	SS	MS	*F*
total	23	3.06207		
treatments	7	3.04910	0.43559	537.28*
error	16	0.01297	0.00081	

LSD = 0.04059 ($P < 0.05$), equivalent to significance at 91.1% of control or less.

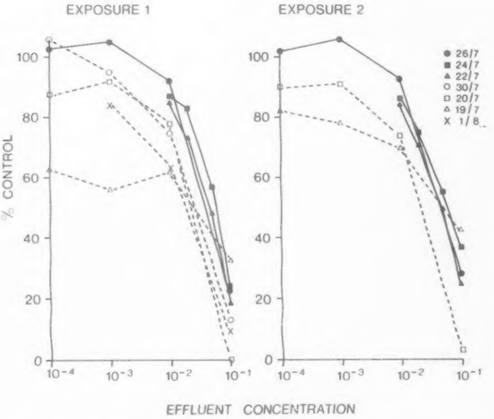

FIG. 3. Phytoplankton carbon uptake (% of control) at four effluent concentrations.

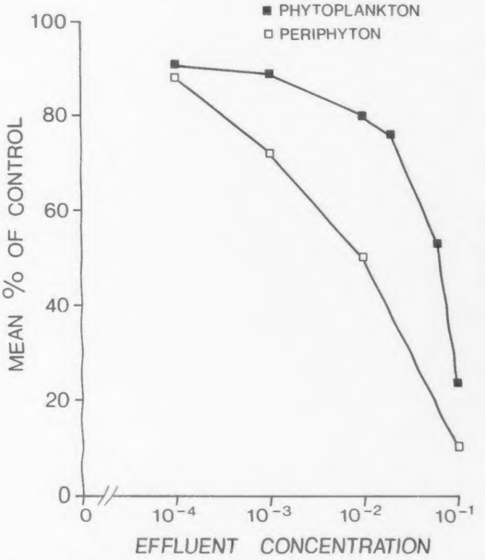

FIG. 4. Carbon uptake (mean % of control) vs. effluent concentration for periphyton and phytoplankton.

each treatment over all experiments, it can be seen (Fig. 4) that, in general, the depression of photosynthetic rate is greater with periphyton than with phytoplankton.

In four of the five experiments there is again a tendency for 4-h rates to be less than 2-h rates for all concentrations other than the 10^{-1} concentration. In four cases the mean square attributable to time (Table 2) is significant. Interaction between time and concentration is also significant in three of these experiments, reflecting a tendency for the per cent of control values to increase with exposure time, particularly at the 10^{-1} concentration.

The results of the pH experiment and accompanying one-way analysis of variance (Table 3) revealed a significant fraction of reduced carbon uptake was due to effluent pH. Reduction in carbon uptake rates observed with effluent having a pH adjusted close to that of the control sample was still large and significant but relatively less than observed with raw effluent. Altering the pH of the control sample also resulted in reduced uptake rates, particularly at the pH corresponding to 10^{-1} raw effluent. The effects obtained with pH adjusted effluent and pH adjusted control appear to combine in a multiplicative fashion to yield the effect of the raw effluent.

TABLE 4. Carbon uptake of *C. erosa* at various effluent concentrations. Results of experiment 1 expressed at % of control.

EXPERIMENT 1

Chemical	Concentration (μg/ℓ) 500	50	5	0.5
Dehydroabietic Acid	90.2	98.4	98.9	99.2
Oleic Acid	105.4	120.4	122.9	—
Guaiacol	117.1	125.5	113.3	122.3
α-terpineol	116.0	117.7	121.1	118.3

EXPERIMENT 2

Chemical	Concentration	% of control
Frozen effluent	10^{-1}	73.7
Frozen effluent	10^{-2}	99.7
Dehydroabietic Acid	500 μg/ℓ	87.0
Oleic Acid	500 μg/ℓ	96.5
Guaiacol	500 μg/ℓ	84.4
α-terpineol	500 μg/ℓ	81.2

LABORATORY EXPERIMENTS

When *Cryptomonas erosa* was subjected to the effluent and various chemicals (Table 4), photosynthesis was stimulated at all concentrations of all chemicals except dehydroabietic acid which depressed photosynthesis at the highest concentration. In the second experiment frozen effluent reduced productivity at the highest concentration while all compounds except oleic acid were slightly inhibitory.

Discussion

Results of this study indicated the periphyton and phytoplankton occurring in Nipigon Bay were extremely sensitive to kraft mill effluent, with concentrations as low as 10^{-4} inhibiting photosynthetic rates measured over the first 2–4 h of exposure. At high concentrations pH elevation accounts for a significant portion of this effect. The remainder of the effect may be due either to toxic components of the effluent or to reduction in available light because of the effluent's very dark color. Stockner et al. (1975) found the latter to be a major factor in depressing areal production rates determined in situ in an effluent plume. In this study the light factor must be discounted since coloration was evident only in the 10^{-1} treatment and even there only as a yellowish tinge. The depression in photosynthetic rates must therefore be attributed to effluent toxicity.

The identities of the compounds in kraft mill effluent toxic to freshwater algae have not to date been investigated. The outcome of the experiments with *Cryptomonas* was inconclusive. Of the compounds tested, only dehydroabietic acid could be said to be consistently toxic. Although this statement rests on the results of only two experiments, it is at least consistent with the results reported for fish by Leach and Thakore (1973) who found that 80% of the toxicity to coho salmon was due to three resin acid soaps including sodium dehydroabietate. Inhibition of photosynthesis observed in the *Cryptomonas* experiments was minor relative to field results, even though the highest levels of the compounds employed were chosen to represent a concentration of 10^{-1} or greater of their average concentrations in the raw effluent (Fox 1977). It therefore seems unlikely that these classes of compounds are responsible for the high degree of toxicity observed in the field.

Since samples of frozen effluent failed to behave in the laboratory as in the field it is possible that the majority of the toxicity observed was due to labile or volatile substances. The latter possibility is suggested by the work of Rainville et al. (1975) who found toxicity of kraft mill wastes to *Coccochloris elebans* in short-term bioassays was significantly reduced or eliminated by aeration or storage of the effluent. It is therefore conceivable that the extreme sensitivity observed in the field experiments was due to enclosure of effluent dilutions in bottles and would not have been observed in the effluent plume itself.

The data indicate that a significant reduction in photosynthesis occurred consistently at an effluent concentration of 10^{-2}. Conclusions regarding the impact this is likely to have on Nipigon Bay are difficult to draw because of the limitations of short-term bioassays. The experimentation employed in this study assumes that the toxic effects of the effluent are limited to the area of the plume having an effluent concentration of 10^{-2} or greater, the algae immediately recovering their normal functional state beyond this area. The area thus affected would only be approximately 2 km^2 (Minns 1977) compared to the 480 km^2 of Nipigon Bay. The experiments cannot predict recovery time, and immediate recovery is unlikely. Mortality and long-term sublethal effects also cannot be estimated and the net result, if any, attributable to any one or combination of the above would be to further increase the zone of influence.

BRAY, G. A. 1960. A simple efficient liquid scintillator for counting aqueous solutions in a liquid scintillation counter. Anal. Biochem. 1: 279–285.

ELORANTA, V., AND P. ELORANTA. 1974. Influence of effluents of sulphite cellulose factory on algae in cultures and receiving waters. Vatten 1: 36–48.

FOX, M. E. 1977. Persistence of dissolved organic compounds in kraft pulp and paper mill effluent plumes. J. Fish. Res. Board Can. 34. (This issue)

GUILLARD, R. R. L., AND C. J. LORENZEN. 1972. Yellow–green algae with chlorophyllide c. J. Phycol. 8: 10–14.

LEACH, J. M., AND A. N. THAKORE. 1973. Identification of the constituents of kraft pulping effluent that are toxic to juvenile coho salmon (*Oncorhynchus kisutch*). J. Fish. Res. Board Can. 30: 479–484.

MINNS, C. K. 1977. Analysis of a pulp and paper mill effluent plume. J. Fish. Res. Board Can. 34. (This issue).

RAINVILLE, R. P., B. J. COPELAND, AND W. T. MCKEAN. 1975. Toxicity of Kraft mill wastes to an estuarine phytoplankter. J. Water Pollut. Control. Fed. 47: 487–503.

STOCKNER, J. G., D. D. CLIFF, AND K. MUNRO. 1975. The effects of pulp mill effluent on phytoplankton production in coastal waters of British Columbia. Fish. Mar. Serv. Res. Dev. Tech. Rep. 578: 1–99.

TIPPET, R. 1970. Artificial substrates as a method of studying populations of benthic micro-algae in fresh water. Br. Phycol. J. 5: 187–199.

WETZEL, R. G. 1965. Necessity for decontamination of filters in ^{14}C measured rates of photosynthesis in fresh waters. Ecology 46: 540–542.

Filtering Rate Performance of *Daphnia retrocurva* in Pulp Mill Effluent[1]

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COOLEY, J. M. 1977. Filtering rate performance of *Daphnia retrocurva* in pulp mill effluent. J. Fish. Res. Board Can. 34: 863–868.

Laboratory experiments were carried out with radioactive *Scenedesmus* to determine the effect on filtering rate of *Daphnia retrocurva* of exposure to different dilutions of raw pulp mill effluent in lake water. Filtering rate decreased progressively as the exposure time in 5 and 10% effluent increased. Most animals seemed able to recover from brief exposures, but with increased time spent in effluent, larger proportions of the animals did not filter when the food was presented.

COOLEY, J. M. 1977. Filtering rate performance of *Daphnia retrocurva* in pulp mill effluent. J. Fish. Res. Board Can. 34: 863–868.

Nous avons fait des expériences en laboratoire avec des *Scenedesmus* radioactifs dans le but de déterminer l'effet, sur le taux de filtration de *Daphnia retrocurva*, d'une exposition à différentes dilutions d'effluent non traité de moulin de pâte dans de l'eau de lac. Le taux de filtration diminue progressivement à mesure qu'augmente l'exposition dans 5 et 10% d'effluent. La plupart des animaux semblent capables de se rétablir après de brèves expositions, mais à mesure qu'augmente la durée d'exposition à l'effluent, de plus grandes proportions d'animaux ne filtrent pas quand on leur présente de la nourriture.

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MOST studies on water quality as indicated by the phytoplankton and zooplankton usually involve the collection, preservation, and enumeration of organisms from "stressed" and "unstressed" areas. This popular approach often leads to results that are hard to interpret due to the unavoidably large, natural sampling variations. Moreover, collections of preserved material can never yield information on the effect the stressing agent has on a species at a particular instant in time. Measurements that quantify the organisms' responses to a perturbation, while usually more difficult and costly to obtain, could add a valuable insight. Although both types of information have been collected for the most abundant zooplankter *Daphnia retrocurva*, the main purpose of this paper is to relate changes in measured filtering rate to pulp mill effluent concentration.

Materials and Methods

In the laboratory, three experiments were carried out between July 26 and August 8, 1974 to determine the effect that pulp mill effluents have on the well being of zooplankton. In these, filtering rates of *Daphnia retrocurva* were measured in concentrations of raw pulp mill effluent ranging from 5 to 40% in uncontaminated or "control" Nipigon Bay water. This water and the experimental animals were taken from an uncontaminated section of the bay from the top 5 m.

All filtering rate determinations were carried out in 1-ℓ Nalgene® bottles. Prior to the experiment, zooplankton were concentrated approximately 3× in a large garbage pail. This was done by adding the filterable contents (75 μm Nitex®) of two 30-ℓ trap samples to 30 ℓ of unfiltered lake water. This was necessary because natural concentrations of zooplankton were too low for the experiments planned. One litre of water was scooped from the pail and filtered through a 200 μm mesh, and the animals were backwashed into an experimental bottle. The animals were allowed at least ½ h to "settle down" after being rinsed into the experimental bottle and before pulp mill effluent was added. Treatment procedures for each of the experiments are summarized in Table 1. Next, exactly 1 ml of ^{14}C labelled, axenically grown, *Scenedesmus quadricauda* culture (3 to 10×10^{8} cells/ml) was added at zero time and after

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

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TABLE 1. Treatment procedure for three laboratory experiments relating filtering rate of *Daphnia retrocurva* to time of exposure to various pulp mill effluent concentrations. Temperature, conductivity, and pH are given for concentrations at time zero. The numbers in the table under time of exposure refer to replicate 1-ℓ bottles.

					Time of exposure to treatment before *Scenedesmus* added (*h*)				
Expt.	pH	Conductivity (*μmhos*)	Temp. (°*C*)	Conc. of effluent added	0	1	2	4	24
1	8.2	106	19	Control	4				
	8.4	120	19	5%	4				
	8.6	143	19	10%	4				
2	8.0	88	18	Control	2			2	2
	8.4	114	18	5%	2			2	2
	8.6	141	18	10%	2	2	2	2	2
3	8.1	107	20	Control	2		2	2	
	8.3	126	20	5%	2	2	2	2	
	8.4	143	20	10%	2		2	2	
	8.3	183	20	20%	2				
	8.7	269	20	40%	2		2		

1, 2, 4, or 24 h. The resultant activity of the water in which the zooplankton fed was determined from triplicate aliquots taken from the radioactive algae and ranged from between 4,800 to 21,500 dmp/ml of feeding suspension. The zooplankton were allowed to feed for 5 min and then filtered onto a 200 μm mesh, anaesthetized in soda water and backwashed into a bottle with a 4% solution of formalin.

In addition to these laboratory experiments, a number of filtering rate determinations were performed in situ using a 10-ℓ Haney type grazing chamber (Haney 1971). In these experiments, 2 ml of ^{14}C *Scenedesmus* containing approximately 4 to 7 × 10^6 cells were released from the piston when the doors of the chamber were closed by the messenger. The trap was utilized in essentially the same manner as described by Haney (1971) except that the filtered samples were stored in 4% formalin instead of storage in a dry state.

To determine animal activity, each animal was placed on a wet 2.1 cm glass fiber filter paper allowing easier transfer to a scintillation vial. One-half millilitre of the tissue solubilizer NCS (Amersham Searle Corp.) was added and the vial heated overnight in a 45°C oven. The next day 10 ml of the fluor PCS (Amersham Searle Corp.) was added to the vial prior to being shaken for an hour. The radioactivity of each animal was determined over a 20-min counting period in a Nuclear Chicago Unilux II liquid scintillation counter (Amersham Searle Corp.). Final activities were determined using the channels ratio method. Prior to digestion, the length of each *Daphnia retrocurva* was determined with an ocular micrometer as the distance from the middle of the eye to the base of the tail spine.

To insure that all the radioactivity in the filtering zooplankters came from ingested *Scenedesmus* particles, the entire sample was washed in a 200 μm mesh under a gentle stream of tap water for several minutes. Four to six adult *Diacyclops bicuspidatus thomasi* copepodites were picked. Since these instars do not filter appreciably, their activity should be close to background. If this was not the case, then the entire sample was rewashed until these animals showed background levels. Individual filtering rates expressed as milliliters filtered/animal per day were determined using the following formula:

$$\underset{\text{(ml/animal per day)}}{\text{Filtering rate}} = \frac{\text{dpm/animal}}{\text{dpm/ml of feeding suspension}} \times \frac{1440}{\text{feeding time in minutes}}$$

When sufficient animals were available from a particular treatment, the relation between filtering rate and size was fitted to the geometric curve $Y = aX^b$ (Burns and Rigler 1967) where Y = filtering rate in ml/animal per day, X is length in mm, a and b are constants fitted from results for each concentration of effluent and for "control" water. In most cases a given regression was determined from animals isolated from replicate bottle dilutions. Animals that did not have measurable filtering rate were not included in the regression calculations and are treated separately elsewhere in this report.

Because of large variations in individual filtering rates and the difficulty in obtaining enough animals from a particular treatment to obtain statistically significant regressions, it was decided to express the results of each treatment as a mean filtering rate for an animal of standard size. The size chosen was 0.74 mm since this was the average size of *Daphnia retrocurva* in the lake at the time of study. For each treatment, size and filtering rate data were fitted to a geometric curve. The calculated slope and intercept from this "best fit" were then used to estimate filtering rate for a 0.74 mm animal.

Results

When the results from the three laboratory experiments are considered together it appears that filtering rate of *Daphnia retrocurva* was negatively affected by both increased exposure time in the effluent and increased effluent concentration.

The results from the first lab experiment are summarized in Fig. 1. Mean filtering rates were similar in 5 and 10% effluent but were depressed 23% relative to the control (Fig. 1B). The proportion of animals which had no measurable filtering rate are similar in all instances (Fig. 1C). This conclusion is supported statistically since the three regression lines are significant at the 5% level but there is no significant difference between the slopes. An analysis of the adjusted treatment means reveals that the 5% treatment is significantly different from the control ($t = 2.761$, 162 df, $P = 0.01$) as is the 10% from the control ($t = 2.473$, $P = 0.025$). There is no significant difference between the 5 and 10% regression lines.

In Experiment 2, the length of exposure to the two effluent concentrations was increased to include filtering rate determinations after 1, 2, 4, and 24 h. The results (Fig. 2) showed that the mean filtering rates of control animals were very similar at all times. These values were, in turn, similar to the time zero estimate in 5% effluent but the rate dropped initially, in the 10% effluent. Panel C shows a time course of filtering rates after several different exposure times in 10% effluent. After the initial drop, little change was observed over the first 2 h. After 4 h another drop was recorded and another after 24 h. The last was 87% lower than the controls.

In the 5% time series (panel D, Fig. 2) the results are different. While there was no immediate measureable effect at time zero, after 4 h a 41% drop was evident but after 24 h the mean filtering rate was back to the control value. This latter result suggests a recovery, perhaps due to settling out of the effluent through the night. A serious depletion of the food source would tend to increase filtering rate and could also partially explain the increases observed in the 5% and control runs.

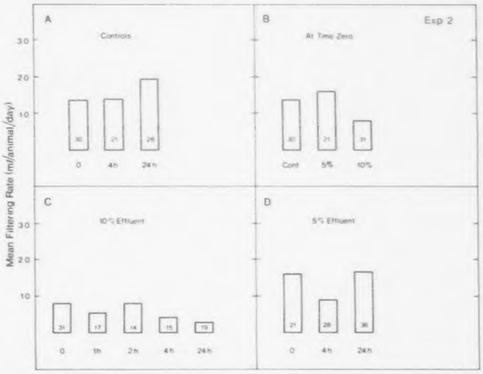

FIG. 2. Filtering rate determinations in Experiment 2 for several effluent concentrations at various times after time zero. The number inside histograms refer to sample size.

The results of the different treatments performed in Experiment 3 are consistent with those of Experiment 2 (Fig. 3). At time zero, the mean filtering rate in the 5% effluent was actually slightly higher than the control while the 10, 20, and 40% concentrations were depressed. After 4 h of exposure in 5% effluent, once again there was a noticeable depression in filtering rate, with even greater drops in the 10 and 40% bottles, the

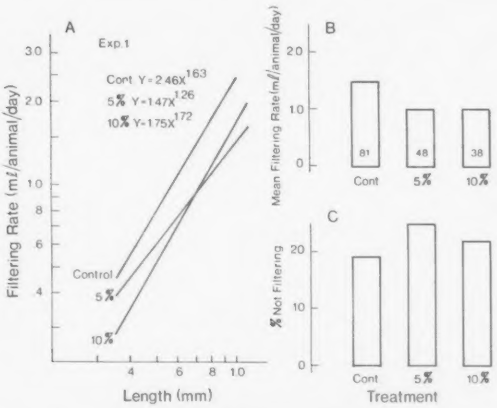

FIG. 1. Filtering rate determinations in Experiment 1 for several effluent concentrations at time zero. The numbers inside histograms refer to sample size.

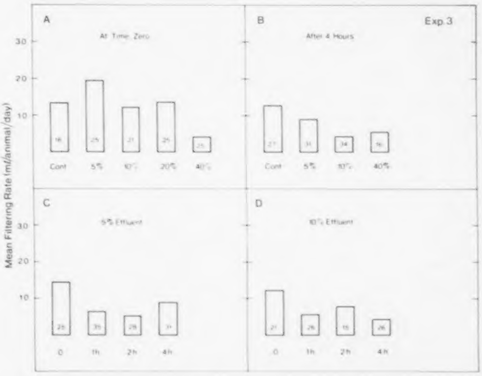

FIG. 3. Filtering rate determinations in Experiment 3 for several effluent concentrations at various times after time zero. The numbers inside histograms refer to sample size.

latter being 57% lower than the corresponding control. There was a sequential drop in mean filtering rate in the 5% time series bottles over the first 2 h with an apparent slight recovery after 4 h. A decrease was observed over 4 h in the 10% effluent.

All of the previous mean rates were calculated excluding those individuals that did not have a measureable filtering rate. At time zero in Experiment 3 (Fig. 4A) there was a progressive increase from 0 to 25% of these animals as effluent concentrations increased. However, control bottles after 4 h showed approximately the same percentage of these types as did the treatment concentrations. These results are somewhat contradictory and imply that animals may not filter as a result of handling procedures as well as treatment. In Fig. 4B, a time course of nonfiltering animals is illustrated over a period of 24 h in 10% effluent. The results are consistent with the hypothesis that prolonged exposure to the effluent disrupts the filtering capacity.

It would be desirable to measure in situ filtering rates inside and outside the effluent plume even though interpretation of data would be most difficult because nothing would be known about the history of the zooplankters collected in these samples and because plume characteristics which in turn would affect interstation comparisons would also be difficult to define.

In spite of these problems, a number of samples were analyzed for filtering performance in a Haney type grazing chamber. At a "control" station in the middle of the bay, individual filtering rates were estimated for 55 animals at 2.0 m. A fit of these individual rates to a geometric curve was not statistically significant, even when these data were grouped as discussed previously. The filtering rates overall were greater than in the control situations of the laboratory experiments with an estimated 0.74 mm daphnid filtering 2.97 ml/day, almost twice most control values from experiments 1 to 3 even though the water temperature was approximately 4 deg. C cooler. This increased filtering rate could be due to lower particle abundance and is probably more indicative of natural daytime filtering rates by *D. retrocurva* in Nipigon Bay since overall particle abundance was increased by approximately 500 *Scenedesmus* cells/ml in the laboratory experiments.

Over 100 individuals were picked from the control station from in situ grazing experiments but none had zero filtering rates. This observation supports the interpretation that rough handling during the laboratory experiments could have been responsible for some of the zero filtering rates recorded.

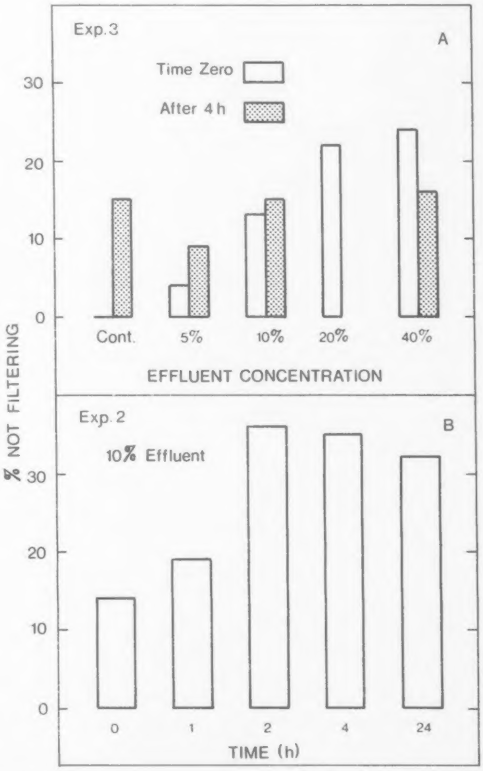

FIG. 4. Percentages of *Daphnia retrocurva* with zero filtering rates from Experiments 2 and 3.

In another in situ grazing experiment done on the same day at 2 m near the mouth of the discharge canal, only 10 daphnids were found in the sample and 2 of these had zero filtering rates. The estimated filtering rate of a 0.74 mm animal from the fitted data would be only 0.83 ml/day even though the water was 2 deg. C warmer than at the control station. This approximate 72% drop in overall performance and the presence of nonfilterers would seem to be directly attributable to the plume.

Discussion

The assumptions involved in determining filtering rates in the manner described have been discussed in numerous publications (for a good summary see Rigler 1971). There are many variables which can affect the calculated filtering rate of zooplankters such as *Daphnia retrocurva* including size, temperature, particle abundance, physiological state at the time of the experiment,

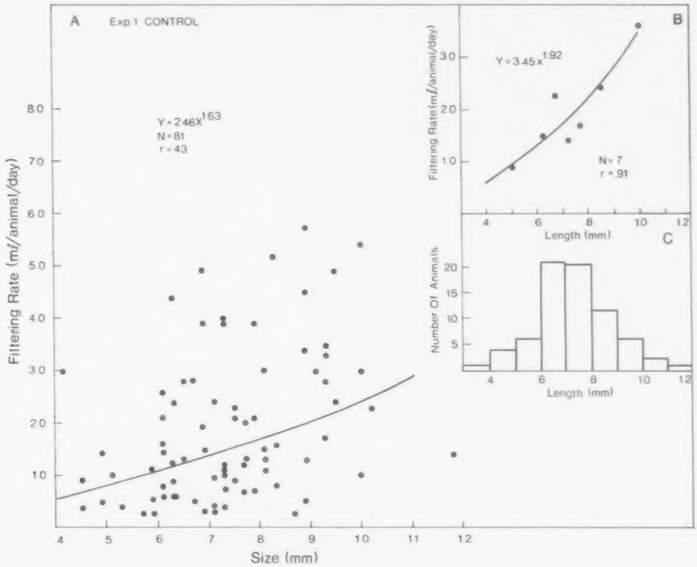

FIG. 5. Filtering rates of *Daphnia retrocurva* from "Control" bottle in Experiment 1. A, Individual filtering rates plotted versus size; B, Group mean filtering rates of the data in A fitted against mean size; C, Frequency plotted against size for the *Daphnia retrocurva* population in Nipigon Bay.

possibly acclimation period, food type, and time of exposure to radioactive food source. Because of these possibilities, it cannot be inferred that the filtering rates calculated from the bottle experiments apply to animals feeding under "natural" conditions. However, differences in filtering rates in a given experiment where only time of exposure and effluent concentration were intentionally varied in several combinations can, with limited confidence, relate to these two variables in terms of cause and effects.

Ideally a curve relating size and filtering rate would have been produced for each treatment. This was not possible for the following reasons. Individuals exhibit a large variation in filtering rate and consequently many individuals would have to be measured in order to develop a relationship with acceptable confidence limits. The individual variation is illustrated in Fig. 5A where data for 81 animals from Experiment 1 in control situations are shown. Despite the large variance, the equation shown in Fig. 5A is statistically significant at the 1% level. If these data are assembled by size into groups with approximately equal numbers and mean size and filtering rate calculated, another curve can be obtained which is also statistically significant (Fig. 5B). The latter regression closely approximates the way most filtering rate/size curves in the literature are generated. This result however leads to the overestimation of filtering rates since for a fixed size of animals they exhibit logarithmic distribution and the variance increases with size.

The results from each of the three lab experiments should be interpreted separately because the chemical characteristics used in the dilutions can change depending on plant activity. Plant effluent contains many complex organic compounds (Fox 1977) any of which could contribute to the observed depressed activity.

Since individuals were picked from the experimental bottles over the course of a year and a half, it was necessary to show that this storage time of the animals in formalin does not affect the subsequent individual activities measured by the scintillation counter. Table 2 contains the results of an analysis of covariance of calculated individual filtering rates picked from replicate bottles in Experiment 1 at three different times. The three groups of 31, 33, and 17 individuals were picked in November 1974, January and November 1975, respectively. While there is much variation in the data, the slopes and intercepts of each of the regressions fitted to a geometric curve are not significantly different from each other.

It would be erroneous to compare the results from these feeding studies to some of the litera-

TABLE 2. A comparison of regression lines[a] relating filtering rate to length for samples analyzed at varying intervals after preservation.

Group[b]	N	Regr. coef.	Deviations from regression df	SS	MS
1	31	1.02	29	18.267	0.630
2	33	1.66	31	14.225	0.459
3	17	2.83	15	11.669	0.778
Between	81	1.59	77	45.382	0.589
Difference between slopes			2	1.221	0.611
Between and Within	80	1.63	79	48.099	0.609
Between adjusted means			2	2.717	1.359

Comparison of slopes: $F = 1.037$ (df = 2,77)
Not Signif. at $P = 0.10$
Comparison of Intercepts: $F = 2.305$ (df = 2,77)
Signif. at $P = 0.10$, NS at $P = 0.025$

[a] ln/ln regressions.

[b] Group 1 = animals from Bottles 1 and 2, picked November 1974; Group 2 = animals from Bottles 2 and 3, picked January 1975; Group 3 = animals from Bottle 4, picked November 1975.

ture values from experiments where great care was taken to control variables that could significantly influence interpretation of the results. The data in this study are intended primarily to show trends relating pulp effluent to the performance of an important bodily function for a common freshwater zooplankter. Filtering rate was chosen as the performance activity because it is relatively simple to measure, but the large variances in individually measured filtering rates necessitated the use of overall group means for intertreatment comparisons. The experiences of this initial approach will be useful in designing future studies concerned with relating environmental perturbations to population well being.

Zero filtering rates, which may indicate mortality, apparently increased with increasing concentrations of effluent and over prolonged periods of exposure but after 24 h in a 10% concentration of effluent, approximately two-thirds of the test animals were still filtering, although performance was much reduced. It cannot be stated with certainty that this was only a result of the effluent, since in that period of time, bottle effects could influence performance. Direct and conclusive evidence that *Daphnia* can recover fully from short-term entrainment in low concentrations of effluent is not available from this study but circumstantial evidence implies this may be so. In any case, averages of only 0.05 and 0.11 km^2 of nearshore water can be expected to have plume effluent concentrations of greater than 20 and 10%, respectively (Minns 1977). Therefore it seems likely that only a very small portion of the zooplankters in the immediate vicinity of the discharge canal would suffer irreversible effects from the effluent. Entrainment into concentrations less than 5% for shorter periods of time might affect larger numbers of plankton but it is unlikely that the animals themselves could not recover.

All of the data collected in this very narrow study suggest the direct effects to the whole zooplankton in Nipigon Bay are very limited.

Acknowledgments

Invaluable assistance in both the field and laboratory were provided by C. Charlton, A. French, D. Gorny, and J. Dunlop. Dr C. K. Minns provided statistical and computer expertise necessary in analyzing the data. Thanks are extended to Domtar Canada Ltd. for their enthusiastic on-site support and to Drs R. Peters and J. Confer for critically reviewing the manuscript.

BURNS, C. W., AND F. H. RIGLER. 1967. Comparison of filtering rates of *Daphnia rosea* in lake water and in suspensions of yeast. Limnol. Oceanogr. 12: 492–502.

FOX, M. E. 1977. Persistance of dissolved organic compounds in kraft pulp and paper mill effluent plumes on the north shore of Lake Superior. J. Fish. Res. Board Can. 34. (This issue)

HANEY, J. F. 1971. An *in situ* method for the measurement of zooplankton grazing rates. Limnol. Oceanogr. 16: 970–977.

MINNS, C. K. 1977. Analysis of a pulp and paper mill effluent plume. J. Fish. Res. Board Can. 34. (This issue)

RIGLER, F. H. 1971. Feeding rates. p. 228–255. *In* W. T. Edmondson and G. G. Winberg [ed.]. A manual on methods for the assessment of secondary production in fresh waters. Blackwell Scientific Publications, Oxford and Edinburgh.

Assessment of the Acute Toxicity, Growth Impairment, and Flesh Tainting Potential of a Bleached Kraft Mill Effluent on Rainbow Trout (*Salmo gairdneri*)[1]

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WHITTLE, D. M., AND K. W. FLOOD. 1977. Assessment of the acute toxicity, growth impairment, and flesh tainting potential of a bleached kraft mill effluent on rainbow trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 34: 869–878.

Static and continuous-flow bioassays utilizing juvenile rainbow trout (*Salmo gairdneri*) were conducted on a northern Ontario bleached kraft mill effluent to assess the range of acute toxicity and related sublethal effects. The acute toxicity of the total mill effluent, as determined by static bioassay procedures, ranged from a 96-h LC50 value of 14–49.0% vol/vol. The results of these bioassays depended on testing methodology and effluent treatment systems employed by the mill when samples were collected. Continuous-flow bioassays conducted on the effluent produced 96-h LC50 values of 21.8 and 24.8% vol/vol. Growth rate of juvenile rainbow trout (1–2 g) held under continuous-flow conditions for 18 days was significantly reduced at 6% vol/vol effluent concentration ($P < 0.05$). Flavor of yearling rainbow trout ($\approx$200 g) exposed to 3% effluent for 48 h was significantly impaired ($P < 0.05$). This effluent concentration, the lowest level impairing flavor, represents approximately 0.12 of the 96-h LC50 derived from continuous-flow bioassays. No significant flavor impairment was detected in fish exposed for 144 h to a 2% effluent concentration. Flavor impairment at a 3% vol/vol effluent concentration, the most sensitive sublethal response measured in this study, may also be the most critical response when assessing the economic impact of a kraft mill discharge to a freshwater ecosystem.

WHITTLE, D. M., AND K. W. FLOOD. 1977. Assessment of the acute toxicity, growth impairment, and flesh tainting potential of a bleached kraft mill effluent on rainbow trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 34: 869–878.

Des analyses biologiques dans des conditions statiques et de débit continu avec de jeunes truites arc-en-ciel (*Salmo gairdneri*) ont été effectuées sur l'effluent blanchi d'une papeterie kraft du nord de l'Ontario dans le but d'en évaluer la gamme de toxicité aiguë et les effets sublétaux qui s'y rattachent. La toxicité aiguë de l'effluent total du moulin, telle que déterminée par des analyses biologiques en milieu statique, varie d'une valeur de CL50 après 96 h de 14 à 49.0% vol/vol. Les résultats de ces essais dépendent de la méthode d'analyse et des systèmes de traitement de l'effluent utilisés par le moulin lors de la cueillette des échantillons. Les analyses biologiques avec débit continu effectuées sur l'effluent donnent des valeurs de CL50 après 96 h de 21.8 et 24.8% vol/vol. Le rythme de croissance de jeunes truites arc-en-ciel (1–2 g) maintenues dans des conditions de débit continu pendant 18 jours ralentit de façon significative à une concentration d'effluent de 6% vol/vol ($P < 0.05$). La saveur de truites arc-en-ciel de l'année ($\approx$200 g) exposées à 3% d'effluent pendant 48 h est significativement affectée ($P < 0.05$). Cette concentration d'effluent, le plus bas niveau affectant la saveur, représente environ 0.12 de la CL50 après 96 h observée lors d'analyses biologiques avec débit continu. Nous n'avons pas détecté de changement significatif de saveur chez des poissons exposés pendant 144 h à une teneur de 2% d'effluent. Le changement de saveur à une concentration d'effluent de 3% vol/vol, la réponse sublétale la plus sensible mesurée au cours de cette étude, peut également être la réponse la plus critique lorsqu'on évalue l'impact économique de l'effluent d'une papeterie kraft sur un écosystème d'eau douce.

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SEVERAL authors (Alderdice and Brett 1957; Gordon and Servizi 1974) have described the toxicity to salmonids of bleached kraft mill effluent discharged by coastal mills to marine and estuarine environments. A limited amount of data is available on the toxicity of effluents discharged by Ontario mills to freshwater systems. Howard and Walden (1965) and Sprague and McLeese (1968), utilizing salmonids as the test species, determined 96-h LC50 values of 9.3% and 12–15%, respectively, for unneutralized bleached kraft effluents from interior mills. The difference in tree species pulped by British Columbia coastal mills — sitka spruce, western hemlock, lodgepole pine, and Douglas fir as compared to jackpine, spruce, poplar, and birch for Ontario mills — undoubtedly affects the toxicity of the effluent.

The Canadian federal effluent guidelines (Canada Dept. of Environment 1971) assess discharges from the pulp and paper industry based on acute lethality to rainbow trout (*Salmo gairdneri*). These guidelines stipulate that no degradation of water quality shall result from pulp mill discharges. Ontario provincial statutes (1974) maintain that no discharge shall cause injury or damage to plant or animal life. Interpretation of the above legislation requires that the more sensitive sublethal responses of aquatic organisms be considered when establishing effluent standards, rather than relying solely on acute lethality to rainbow trout.

Reduced growth rates and impairment of flesh flavor of salmonids exposed to low concentrations (<10%) of kraft pulpmill effluents have been described by Warren et al. (1973) and Cook et al. (1971). German (1968) reported tainting in the flesh of walleye taken from Nipigon Bay and resultant market rejections of these fish.

The kraft mill located on Nipigon Bay installed a condensate steam stripper system to treat digester blow gases and evaporator condensates in an attempt to reduce the acute lethality and flesh tainting potential of the total mill effluent. The steam stripping facility was expected to remove volatiles such as hydrogen sulfide, methyl mercaptan, disulfides, methanol, ethanol, acetone, methyl ethyl ketone, and terpenes. Previous studies (Cook et al. 1971; Seppovaara and Hynninen 1970) indicated that these compounds were responsible for a large portion of the toxicity and tainting potential of a pulp and paper effluent and could be effectively removed by steam stripping.

The objective of this study was to determine the range of acute lethality and growth impairment of a northern Ontario bleached kraft mill effluent to juvenile rainbow trout. Upon installation of the steam stripper an additional study was conducted to investigate the occurrence of flavor impairment of the fish flesh after exposure to low concentrations of the total mill effluent.

To determine the most representative procedure for evaluating kraft mill effluent acute toxicity, 96-h static, semistatic (48 h solution replacement) and continuous-flow bioassays were conducted. In an attempt to define the effect of aeration on acute toxicity, static bioassay solutions were continually aerated while semistatic bioassays were periodically aerated with pure oxygen.

Materials and Methods

Rainbow trout (1–2 g) were purchased from a commercial hatchery near Otterville, Ontario and were acclimated to the dilution water at 15°C for a minimum of 2 wk on site prior to use. Mortality was less than 1% for any one week prior to testing. All fish were starved for 24 h prior to testing.

All bioassays were conducted in a prefabricated building adjacent to the mill's combined effluent channel. Effluent was pumped from this channel at a point approximately 80 m upstream of the discharge to Nipigon Bay.

Results of three preliminary range tests indicated that an LC50 for the total mill effluent was between 10 and 50% vol/vol. Subsequent effluent concentrations for acute bioassays were chosen based on these results and operating conditions of the mill at the time of sample collection for each bioassay. All concentrations were tested in duplicate and control fish were exposed to dilution water pumped from a submerged (10 m) intake in Nipigon Bay.

Acute static and continuous-flow bioassays were conducted over a 96-h period and pH, conductivity, and dissolved oxygen content of the test solutions were measured daily. Mortalities were recorded at 0.5, 1, 3, 6, 12, 24, 36, 48, 72, and 96 h. Death of a fish was recorded as lack of opercular ventilation and failure to respond to prodding. Dead fish were removed at once and fork length and wet weight were measured.

Bioassay data were plotted on log-probability paper and 96-h LC50 values were estimated.

ACUTE BIOASSAYS — STATIC

Effluent samples for each static bioassay were obtained by compositing grab samples taken over a 1-h period when the mill was operating under normal conditions. Of the seven static bioassays conducted, five were carried out on site at the mill while effluent samples for two additional bioassays were transported to a central laboratory for evaluation.

On-site testing was initiated within 12 h of collection of the sample. The effluent samples transported to the central laboratory were tested within 36 h.

All samples were maintained at 4°C in sealed 20-ℓ containers until testing. Effluent samples were neither filtered nor neutralized.

Ten-litre test solutions (6–32% vol/vol) were prepared in polyethylene containers and placed in a water bath for temperature regulation. Samples tested on site were diluted with water from Nipigon Bay, whereas testing at the central laboratory utilized dechlorinated municipal tap water for dilution (Table 1). Test temperatures were 15 ± 1°C on site and 12 ± 1°C at the central laboratory. Five fish were randomly placed in each of the effluent concentrations to give a maximum fish loading density of 1.09 g/ℓ.

Samples tested on site were renewed after 48 h. Fresh dilutions were prepared from the original effluent composite and the dilution water for the replacement solutions was vigorously aerated with oil-free air prior to mixing with the effluent. On-site static bioassays were aerated with pure oxygen at 250 ml/min for 2 min after 24 and 72 h. Pre- and posttreatment dissolved oxygen concentrations were measured on each of these occasions. Effluent samples tested at the central laboratory were continuously aerated but there was no solution replacement. All other bioassay procedures conformed to the guidelines as set out in Standard Methods for the Examination of Water and Wastewater (APHA et al. 1971). Prior to each static bioassay, samples of dilution water and effluent were subjected to routine water quality analysis. The results of chemical analysis of total mill effluent samples collected during the static bioassay series, as well as other effluent variables and flow rates as provided by mill personnel, are presented in Table 2. A limited number of samples preserved with zinc acetate and analyzed for H_2S had a mean value of 6.8 mg/ℓ.

ACUTE BIOASSAYS — CONTINUOUS-FLOW

Effluent for continuous-flow bioassays was continuously pumped from the mill's main effluent channel and was maintained at 15 ± 1°C by passing it through 18.3 m of 0.9 cm bore stainless steel tubing immersed in a 1350-ℓ 15°C water bath. The cooled effluent was shunted to a modified proportional diluter (Mount and Brungs 1967) every 2 min, thus exposing the fish to the full range of waste quality resulting from production changes within the mill.

The diluter supplied each of the twelve 100-ℓ glass bioassay vessels at the rate of 265 ± 20 ml/min producing a 90% molecular replacement in 15 h. Test solutions were not aerated. Ten fish were randomly assigned to each of the effluent concentrations and control solutions after the bioassay vessels had attained their selected concentrations.

A commercial monitoring system (Leeds and Northrup) recorded the pH and conductivity of the whole effluent prior to dilution throughout the 96-h exposure period to detect spills.

Samples were taken from each of the effluent concentrations and the control solutions when the fish were placed in the bioassay vessels and again at 48 h. These samples were subjected to routine water quality analysis and resin acid determinations.

TABLE 1. *Physicochemical characteristics of central laboratory and Nipigon Bay dilution water.*

	Central laboratory dechlorinated tap water	Nipigon Bay
Alkalinity as mg·$CaCO_3$/ℓ	89 ± 3.0	68.2 ± 10
EDTA hardness as mg$CaCO_3$/ℓ	139 ± 5.0	69 ± 5.0
Chloride (mg/ℓ)	33 ± 2.0	1.5 ± 0.7
Sulphate (mg/ℓ)	33 ± 3.0	2.7 ± 1.0
Sodium (mg/ℓ)	13 ± 1.0	1.7 ± 0.6
Potassium (mg/ℓ)	1.7 ± 0.6	—
Conductivity (μmhos/cm)	332 ± 15	100.3 ± 6
pH	7.4 ± 0.2	7.8 ± 0.4
Threshold odor	—	12.3 ± 1.3
Residual chlorine (μg/ℓ)	30.1 ± 3.0	—

SUBLETHAL EFFECTS — GROWTH IMPAIRMENT

The study on growth impairment was undertaken prior to the installation of the steam stripper treatment facility at the mill.

Juvenile rainbow trout were acclimated on site to dilution water and test temperature (15 ± 1°C) for a 2-wk period with no significant mortality (<1%).

Prior to exposure, the fish were starved for 24 h, selected for uniform size, lightly anesthetized with tricaine methanesulfonate (MS-222 Sandoz) and weighed to the nearest 0.01 g. Fork length was measured to the nearest 0.1 cm. Twenty fish, about 1.3 g, were randomly placed in each of the twelve 100-ℓ growth aquaria to provide a duplicate population for each of the six treatments; control, 1, 2, 3, 6, and 10% vol/vol effluent. The initial mean weights of all fish stocked in each of the exposure groups were similar ($P < 0.05$).

Before the effluent was introduced into the dilution system, the fish were allowed 24 h to recover from the stress of handling. Introduction of the effluent into the exposure tanks marked day one of the exposure period.

The fish were fed four times daily on "Ewos" trout starter pellets at a ration level of about 8% wet weight per day except for a 24-h period before they were weighed and measured. This ration level was maintained throughout the exposure. Accumulated feces and excess food were removed from the tanks each day prior to the initial feeding.

The aquaria were artificially illuminated with a combination of fluorescent and incandescent lights for a 16-h photoperiod. A light controller (Drummond and Dawson 1970) maintained a dawn and

TABLE 2. Total mill effluent characteristics for acute static and continuous-flow bioassays.

Variable[a]	Static	Continuous flow
Na^+	152.9±62.4	115.0±8.6
Cl^-	88.3±69.0	58.3±24.9
$SO_4^=$	151.7±41.3	120.0±26.5
Phenol (μg/ℓ)	807.0±440.0	877.0±109.0
Dissolved solids	720.1±261.7	606.7±27.5
Suspended solids	96.3±52.9	66.7±24.7
Alkalinity	182.1±78.3	123.7±9.1
BOD_5	183.3±76.7	140.0±10.0
COD	542.2±240.1	435.0±63.8
pH	8.36±1.05	8.01±0.35
Conductivity (*μmhos/cm* @ 25°C)	711.3±180.9	700.0±100.0
Flow (*$m^3 min^{-1} \times 10^5$*)	3.2±0.9	3.4±0.6
Na_2SO_4 (*tons/day*)	39.9±5.7	42.9±7.5
BOD_5 (*tons/day*)	16.6±2.7	—
Suspended solids (*tons/day*)	6.8±0.8	6.9±1.4
Dissolved solids (*tons/day*)	53.6±7.7	57.2±9.2

[a]All results reported as mg/ℓ unless otherwise noted.

TABLE 3. Chemical and physical characteristics of effluent dilutions measured during growth study.

Variable[a]	$S^=$	BOD_5	COD	Solids		Phenols (μg/ℓ)	Alkalinity $mgCaCO_3/ℓ$	Hardness $mgCaCO_3/ℓ$	Conductivity (*μmhos/cm*)	pH	Dissolved oxygen	Temp. (°C)
				Susp.	Diss.							
Concentration												
Control	0.02	1.3	23	80	2	2.3	66.5	67	134.4	7.54	9.62	15.48
1%	0.02	2.0	25	82	3	6.5	68	69	140.1	7.61	9.55	15.04
2%	0.035	3.0	15	90	6	10	70	70	142.7	7.64	9.43	14.85
3%	0.05	3.8	33	100	6	17	69.5	69	152.5	7.75	9.55	14.81
6%	0.06	5.3	25	105	8	27	72	71	158.0	7.84	9.44	15.21
10%	0.17	8.0	43	126	12	37.5	74	77	186.8	7.95	9.32	15.41

[a]All results expressed as mg/ℓ unless otherwise noted.

dusk simulation of light intensity. Growth aquaria were randomly placed in the testing area to negate any effect of position within the area. A black polyethylene sheet surrounded the growth aquaria to provide a shield against mechanical disturbances and extraneous sources of light.

For this portion of the study the proportional diluter flow rate was increased to 430 ± 20 ml/min for each aquarium and rechecked at 2-day intervals throughout the experiment. Dissolved oxygen, pH, temperature, and conductivity were measured daily in each of the growth aquaria (Table 3). Samples of the effluent dilutions were collected at 5-day intervals for routine chemical analysis (Table 2).

At the end of an 18-day exposure period the experiment was terminated due to a complete shutdown of all the mill production areas. The fish were starved 24 h prior to the termination, sacrificed with a lethal concentration of MS-222, and weighed to the nearest 0.1 g. Fork length was measured to the nearest 0.1 cm.

Initial and final mean weights for each of the duplicate populations were compared by analysis of independent *t*-distribution. Further statistical analysis attempted to correlate the degree of growth impairment with an increase in effluent concentration.

SUBLETHAL EFFECTS — FLAVOR IMPAIRMENT

Yearling rainbow trout (≃200 g), purchased from the Otterville hatchery, were utilized for the study on flavor impairment. The fish were acclimated for 2 wk at 15 ± 1°C to water pumped from Nipigon Bay. All systems for effluent collection, cooling and dilution were the same as those for all other continuous-flow bioassays. The steam stripper system was operational throughout the exposure period. Duplicate populations of 10 fish each were exposed to final effluent concentrations of 2, 3, 6, 10, and 18% vol/vol plus additional control solutions. The exposure period for fish held in 3, 6, 10, and 18% effluent concentrations was 48 h while additional fish were held in 2 and 3% test solutions for 144 h. Due to the high fish loading rate in this portion of the study all bioassay containers were aerated to maintain dissolved oxygen concentrations above 7 mg/ℓ. Constant replacement of volatile effluent toxicants in this continuous-flow bioassay minimized the stripping

TABLE 4. Toxicity of BKME to juvenile rainbow trout (*Salmo gairdneri*).

Treatment	Loading rate (*gm/ℓ*)	96-h *LC*50 (*% vol/vol*)
Static, aerated[a]	0.869	37.0
Static, aerated[a]	0.499	36.0
Static, nonaerated[b]	0.825	16.5
Static, nonaerated[b]	0.960	14.0
Static, nonaerated[b]	0.750	18.7
Static, nonaerated[b]	0.975	28.0
Static, nonaerated steam stripped[b]	1.09	49.0
Continuous flow nonaerated steam stripped[b]	.337	25.8
Continuous flow nonaerated steam stripped[b]	.427	21.8

[a]Tested at central laboratory.
[b]Tested on site.

potential of continual aeration. The fish were fed "Ewos" trout food pellets throughout the acclimation and exposure periods. At the termination of each portion of the study the fish were sacrificed, sealed in plastic bags and quickly frozen.

The frozen fish were returned to the central laboratory for flavor evaluation. The flavor evaluation tests were conducted according to the taste panel method described by Wells (1972). The presence or absence of foreign flavor as compared with the control was recorded as follows: 0 — absent; + — barely perceptible; ++ — definite; or +++ — strong. All responses in the definite or strong categories were designated as positive responses. One unknown control was always included and several fish were duplicated during each tasting session.

The Mann–Whitney nonparametric ranking test was used to compare taste panel responses to samples from each member of a pair of duplicate effluent concentrations. Chi-square analyses evaluated the incidence of foreign flavor of fish exposed to the effluent compared to the flavor of control fish.

Results

ACUTE BIOASSAYS — STATIC

Continual aeration of static bioassay effluent solutions reduced the acute toxicity by 122%. Three on-site semistatic bioassays conducted prior to the installation of the steam stripper produced a mean 96-h LC50 value of 16.4 ± 2.4% vol/vol (Table 4). These bioassays were not aerated but there was a periodic addition of small volumes of pure oxygen. Two bioassays conducted at the central laboratory with continual aeration and no solution replacement had an increased mean LC50 figure of 36.5 ± 0.5% vol/vol. Aerated effluent dilutions produced a noticeable sulphurous odor for a period of 24–36 h, suggesting that volatile sulphur compounds were being stripped off.

Two additional semistatic bioassays were conducted on-site. The sample for the first bioassay was collected while the stripper facility was inoperative and resulted in an LC50 value of 28.0% vol/vol. The second bioassay conducted with the steam stripper on-line produced an LC50 of 49.0% vol/vol. As all other production variables of the mill were similar when the effluent samples were collected for these two bioassays, there is an indication that the steam stripper may be effective in reducing the acute toxicity of the mill effluent.

Bioassay containers aerated continuously at the central laboratory were held at >90% air saturation throughout the exposure period. Dissolved oxygen levels in the on-site bioassay containers declined somewhat in the highest effluent concentrations (>18% vol/vol), but as a result of 48-h solution replacement and periodic oxygenation, the dissolved oxygen concentration was not less than 4.0 mg/ℓ for longer than 6 h.

During each of the static and semistatic bioassays, fish in the higher (>18% vol/vol) effluent concentrations displayed an initial increased respiratory rate, followed by a loss of equilibrium within the first 48–72 h.

All exposure tank temperatures were constant for the selected range of each of the bioassays. Mean measured pH values for the highest effluent concentrations tended to be alkaline (pH 8.0) but were satisfactory for fish survival.

ACUTE BIOASSAYS — *Continuous-Flow*

A mean 96-h LC50 of 23.3% vol/vol was derived from the results of two continuous-flow bioassays conducted with the steam stripper treatment system in operation. This represents an increase of >100% in the 96-h LC50 in comparison to those values derived from static bioassays conducted on similar steam stripped effluent. Resin acid analysis of total mill effluent collected during these bioassays resulted in a mean concentration of 3.38 ± 1.03 mg/ℓ. Isopimaric acid accounted for 34.8% of the total resin acids detected, while dehydroabietic and abietic acid constituted 11.6 and 26.6%, respectively, of the resin acid content of the effluent.

No major spills or process malfunctions were reported by the mill personnel during the test period. This was evidenced by relatively stable pH and conductivity values for the effluent concentrations measured (Table 2). The mixing action of the diluter system resulted in dissolved oxygen values in excess of 80% saturation for all effluent concentrations tested. There was no noticeable sulphurous odor emitted from even the highest effluent concentrations tested as was noted for the aerated static bioassays. Fish exposed to lethal effluent concentrations (>18% vol/vol) did not usually die until after 72 h of exposure, and before they died, they behaved similarly to those observed in the higher static effluent concentrations.

SUBLETHAL EFFECTS — GROWTH IMPAIRMENT

On termination of the exposure, mean wet weights for all the exposure groups increased but were less than that of the control populations (Fig. 1). Fish exposed to a 6% vol/vol effluent concentration demonstrated a significant reduction in weight increase ($P < 0.05$). Those fish held in 1, 2, and 3% effluent concentrations exhibited no significant decrease in growth rate ($P < 0.05$). Reduced weight gain and effluent concentration were significantly correlated ($r = -0.86, P < 0.01$).

All fish exhibited a rapid and apparent complete recovery from the anesthetic administered during the measurement procedure. After 7 days of exposure, fish held in 6 and 10% effluent concentrations began to show signs of reduced feeding activity and erratic opercular ventilation. On the 10th day of exposure a majority of the fish held in the 10% effluent demonstrated a loss of equilibrium and surface breathing. There was a 65% mortality in this effluent concentration after 16 days of exposure.

During the 18-day exposure period three major spills were detected. When a spill was reported, the waste delivery system was shut down to maintain prespill toxicant levels in the exposure tanks. The dilution system was not put into operation until members of the mill's laboratory staff confirmed that normal production operations had resumed.

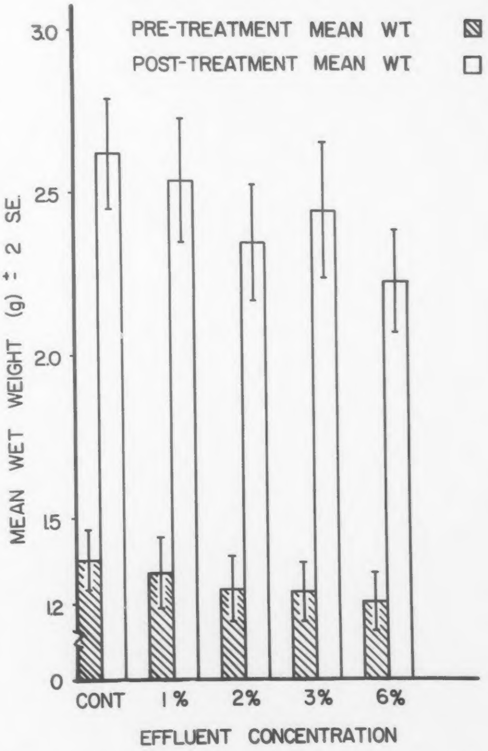

FIG. 1. Mean wet weight changes of juvenile rainbow trout (*Salmo gairdneri*) exposed to sublethal concentrations of BKME.

SUBLETHAL EFFECTS — FLAVOR IMPAIRMENT

Results of the taste panel responses indicated that a definite or strong taint was observed in 50% or more of the fish exposed to effluent concentrations greater than 2% vol/vol (Table 5). Chi-square analysis of the data indicated that after 48 h of exposure, fish in 3, 6, 10, and 18% vol/vol effluent concentrations showed a signifi-

TABLE 5. Incidence of foreign flavor in BKME exposed rainbow trout.

No. of samples	Effluent concentration	Exposure period	Percent positive[a]
36	Control	144 h	19.4
17	18%	48 h	94.1
18	10%	48 h	77.8
18	6%	48 h	50.0
24	3%	48 h	54.2
11	3%	144 h	63.6
12	2%	144 h	16.7

[a] Definite or strong response.

TABLE 6. A comparison of taste panel responses to flesh samples of rainbow trout exposed to BKME for two time periods.

Concentration (% *vol/vol*)	Exposure period	vs.	Concentration (% *vol/vol*)	Exposure period	Level of significance[a]
18	48 h		control	144 h	S.D.
10	48 h		control	144 h	S.D.
6	48 h		control	144 h	S.D.
3	48 h		control	144 h	S.D.
3	144 h		control	144 h	S.D.
2	144 h		control	144 h	N.S.D.
18	48 h		10	48 h	N.S.D.
10	48 h		6	48 h	S.D.
6	48 h		3	48 h	N.S.D.
6	48 h		3	144 h	N.S.D.
3	48 h		3	144 h	N.S.D.
3	48 h		2	144 h	S.D.
3	144 h		2	144 h	S.D.

[a] S.D. — significantly different ($P < 0.05$).

cant ($P < 0.05$) impairment in flavor relative to control fish (Table 6). There was no significant difference in the degree of tainting of fish held in a 3% effluent concentration for 48 h compared to the tainting observed after 144 h. Fish held in 3% effluent for 48 and 144 h showed a significant ($P < 0.05$) impairment in flavor relative to fish exposed to 2% effluent for 144 h. The 3% effluent concentration represents approximately 0.12 of 96-h continuous-flow LC50 of the steam-stripped effluent. Relative to control samples no significant ($P < 0.05$) tainting was identified in fish exposed to 2% effluent for 144 h.

Although the panelists were not evaluating samples from a single fish taken from each one of the exposure concentrations, statistical analysis showed that this factor did not interfere with the interpretation of the data. The results of the Mann–Whitney test revealed that panelists could not distinguish a significant difference in flavor between fish taken from either member of a pair of duplicate effluent concentrations.

Discussion

A comparison of the LC50 values derived from aerated and nonaerated static bioassays reveals a 122% reduction in toxicity for the aerated bioassays. At the time effluent samples were collected for these series of bioassays, mill operating conditions were similar and, except for aeration all other conditions of the bioassays, such as loading rate and temperature, were similar. Thus the decrease in toxicity may be attributed to the oxidation and volatilization of sulphur compounds and other volatile toxicants as a result of aeration.

Aeration, a recognized method of BKME treatment, oxidizes sulphur compounds and this reduces the toxicity of the effluent (Werner 1963). Seppovaara and Hynninen (1970) demonstrated that volatile sulphur compounds could be readily air-stripped from the effluent with a resultant decrease in toxicity. Oxidation by air or steam stripping of BKME containing high concentrations of sulphur compounds significantly reduces the effluent toxicity, but if small quantities of volatile toxicants are present only a minimal reduction in toxicity will result.

When determining the effect of a kraft mill discharge on a local fisheries population, the receiving water conditions must be considered. If a kraft mill effluent is discharged to a well mixed receiving water, volatile toxicants will be rapidly dissipated. If the receiving water is of limited capacity with a low turnover rate the discharge of volatile toxicants will be relatively significant. The kraft mill on Nipigon Bay discharges an effluent with a mean BOD of 16.6 tons per day. The high oxygen demand of this effluent may deplete the dissolved oxygen level of the receiving water in an area immediately adjacent to the outfall. Thus during periods of low flow and lowered oxygen levels nonaerated bioassays may be more relevant in assessing the toxicity of the effluent at that time.

Prior to the installation of the steam stripper, mean measured hydrogen sulfide levels for total mill effluent samples were 6.8 mg/ℓ, an order of magnitude greater than the 120-h LC50 of 0.7 mg/ℓ H_2S for cutthroat trout (*Salmo clarki*) as reported by Haydu et al. (1952). After the stripper was installed, hydrogen sulfide levels were nondetectable in the total mill effluent while

TABLE 7. Effect of kraft mill effluents on growth rate of salmonids.

Author	Species	Effluent type	Concentration (*vol/vol*)	% 96-h LC50	Exposure period (days)	Growth rate effect
Webb and Brett	Sockeye salmon	BKME[a]	25%	(—)	57	Reduced
Webb and Brett (1972)	Sockeye salmon	BKME	1.0% and 2.5%	(—)	57	No effect
Tokar and Owens (1968)	Chinook salmon	UKME[b]	—	(0.09–0.07)	14–18	Increased
Davis and Mason (1973)	Coho salmon	BKME	—	(0.2–0.05)	50	Increased
McLeay and Brown (1974)	Coho salmon	BKME	—	(0.25–0.1)	50	No effect
McLeay and Brown (1974)	Coho salmon	BKME	—	(0.25)	200	Increased

[a] BKME — Bleached kraft mill effluent.
[b] UKME — Unbleached kraft mill effluent.

sulfate concentrations were reduced by 50% to 100 mg/ℓ, the minimum lethal concentration reported by Haydu et al. (1952) for a species of minnow.

The toxic action of sulfur compounds may involve respiratory failure and suffocation. Hydrogen sulfide binds to the metal constituents of enzymes and hence inhibits the iron-containing cytochrome C-enzyme in the respiratory chain (Werner 1963). Seppovaara and Hynninen (1970) stated that toxic effects of sulfides and mercaptans result in the reduced ability of red blood cells to transport oxygen. In all bioassays conducted with and without continued aeration, dissolved oxygen content of the effluent dilutions did not fall below 4.0 mg/ℓ. Visual observations of fish in lethal concentrations indicated severe respiratory stress prior to death. Therefore, a portion of the toxicity of the effluent may be attributed to the inability of the fish to utilize available oxygen.

Although no deaths in the higher effluent concentrations could be attributed directly to anoxia, the stress placed upon the fish due to diminished oxygen levels for portions of the test period would decrease their tolerance to other toxicants present in the waste.

Leach and Thakore (1973) identified some of the nonvolatile constituents of kraft pulping effluent that were acutely toxic to juvenile coho salmon (*Oncorhynchus kisutch*). They determined that 80% of the effluent's toxicity was attributable to resin acid soaps. Mean resin acid levels measured in lethal effluent concentrations of continuous flow bioassays were within the lethal threshold range of 1–3 mg/ℓ (Leach and Thakore 1973).

A comparison of the results derived from continuous-flow and on-site static bioassays with 48-h solution replacement indicates that the continuous-flow method consistently yielded higher toxicity values. Loch and MacLeod (1974) investigating the acute lethality of several kraft mill effluents indicated that flow-through bioassays appeared to be at least fourfold more sensitive than static bioassays. Results from the Nipigon Bay study suggest that continuous-flow bioassays are more than twice as sensitive as "semistatic" (48-h solution replacement) bioassays even when the steam stripper facility is operating. Continuous-flow bioassays are most costly to set up, require considerably more effluent than static bioassays, and necessitate on-site testings, but they provide a more representative profile of kraft mill effluent toxicity. The continual solution replacement of flow-through bioassay reduces the extent to which the toxicants may be depleted by volatilization and adsorption.

Responses of fish to sublethal levels of contaminants, such as growth impairment or the production of an unnatural flavor in fish flesh, are critical to the existence of a fishery or the marketability of a commercial fishery.

The mean weight increase of fish in exposure tanks receiving 3% vol/vol BKME was less than but not significantly different from the weight increase observed for the control groups but greater than that of fish held in 2 and 6% effluent concentrations. This result suggests that a slight growth stimulation may have occurred in the 3% effluent concentration. Other authors have observed growth reduction and stimulation in salmonids after exposure to low concentrations of BKME (Table 7). Warren and Davis (1967) suggested that a reduction in growth rate on exposure to sublethal concentrations of BKME may be a result of a decrease in either food intake, assimilation efficiency, metabolic processing, or an increase in maintenance requirements. A preliminary study by Webb and Brett (1972) demonstrated that oxygen consumption was elevated by a factor of about two in effluent concentrations as low as 1% of the 24-h LC50. Thus, it has been postulated that exposure to sublethal concentrations of BKME may result in elevation of maintenance energy requirements and thus reduce the proportion of energy available for growth.

Tokar and Owens (1968) and McLeay and

Brown (1974) have reported growth stimulation in salmonids on exposure to low effluent concentrations of from 0.07 to 0.25 of the 96-h LC50 value. They have suggested that the dark color of the effluent may reduce interaction between fish, thus decreasing aggression and reducing the maintenance requirements of the fish. This would increase the energy available for growth. McLeay and Brown (1974) stated that kraft mill effluents may contain minimal amounts of growth increasing factors (hormone analogs) derived from the wood extractives. These authors also discussed the possibility that the salinity of certain effluent concentrations provided optimum osmotic conditions for maximum growth.

The extent of a fisheries tainting problem in an area is difficult to quickly assess since the tainted fish appear normal on gross inspection. Organoleptic testing is the only proven means of accurately defining the degree of flavor impairment. Whole fish may be used for flavor evaluation (Shumway 1968) or samples may be taken from specific areas of the fish (Wells 1970; Swabey 1964). Baldwin et al. (1969) could not detect any flavor difference in samples taken from various areas of the body.

Tainting compounds may originate from either natural sources or industrial discharges. Thaysen and Pentelow (1936) reported that a type of *Actinomyces* could produce an "earthy" pungent odor in water and result in the tainting of fish. The results of the threshold odor determinations conducted on the Nipigon Bay dilution water (Table 2) suggests that the tainting observed was not a result of natural sources.

Results of the Nipigon Bay study indicate that once a fish has become tainted, an increase in the length of the exposure period at that concentration does not seem to intensify the taint. Also, if an effluent concentration does not taint the fish in a short time period, increasing the exposure period threefold will not impair flavor.

The 3% effluent concentration, the lowest level found to produce a flavor impairment, was approximately 0.12 of the 96-h continuous-flow LC50 of the steam-stripped effluent. A study by Cook et al. demonstrated the tainting threshold of a kraft mill employing a steam stripper varied between 0.5 and 0.3 of the incipient LC50.

The most sensitive sublethal response measured in this study, flavor impairment at a 3% vol/vol effluent concentration, may be the most critical response when assessing the economic impact of a kraft mill discharge to a freshwater ecosystem.

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ALDERDICE, D. F., AND J. R. BRETT. 1957. Some effects of kraft mill effluent on young pacific salmon. J. Fish. Res. Board Can. 14: 783–795.

AMERICAN PUBLIC HEALTH ASSOCIATION, AMERICAN WATER WORKS ASSOCIATION, AND WATER POLLUTION CONTROL FEDERATION. 1971. Standard methods for the examination of water and wastewater. 13th ed., Washington, D.C. 874 p.

BALDWIN, R. E., K. G. SIDES, AND J. W. ROBINSON. 1969. Relationship of size and body area to the flavor and aroma in fish. Trans. Am. Fish. Soc. 98: 533–537.

CANADA DEPARTMENT OF THE ENVIRONMENT. 1971. Water pollution control directorate. Pulp and paper effluent regulations. Regulations, codes and protocols. Rep. 1: 7 p.

COOK, W. H., ET AL. 1971. The effect of pulp and paper mill effluent on the taste and odor of fish. CPAR Rep. 12-2. Can. For. Serv. 191 p.

DAVIS, J. C., AND B. J. MASON. 1973. Bioassay procedures to evaluate acute toxicity of neutralized kraft pulp mill effluent to pacific salmon. J. Fish. Res. Board Can. 30: 1565–1573.

DRUMMOND, R. A., AND D. W. F. DAWSON. 1970. An inexpensive method for simulating diel patterns of lighting in the laboratory. Trans. Am. Fish. Soc. 99: 434–435.

GERMAN, M. J. 1968. Biological survey of Nipigon Bay. Ont. Water Resour. Comm. Rep. 17 p.

GORDON, R. W., AND J. A. SERVIZI. 1974. Acute toxicity and detoxification of kraft pulp mill effluent. Int. Pac. Salmon Fish. Comm. Rep. 31.

HAYDU, E. P., H. R. AMBERG, AND R. E. DIMICK. 1952. The effect of kraft mill waste components on certain salmonid fishes of the Pacific northwest. Tappi 48: 136–141.

HOWARD, T. E., AND C. C. WALDEN. 1965. Pollution and toxicity characteristics of kraft pulp mill effluents. Tappi 48: 135–141.

LEACH, J. M., AND A. N. THAKORE. 1973. Identification of the constituents of kraft pulping effluents that are toxic to juvenile coho salmon (*Oncorhynchus kisutch*). J. Fish. Res. Board Can. 30: 479–484.

LOCH, J. S., AND J. C. MACLEOD. 1974. Factors affecting acute toxicity bioassays with pulp mill effluents. Fish. Mar. Serv. Cent. Reg. Tech. Rep. Ser. CEN/T-74-2: 14 p.

MCLEAY, D. J., AND D. A. BROWN. 1974. Growth stimulation and biochemical changes in juvenile coho salmon

(*Oncorhynchus kisutch*) exposed to bleached kraft pulp mill effluent for 200 days. J. Fish. Res. Board Can. 31: 1043–1049.

Mount, D. I., and W. A. Brungs. 1967. A simplified dosing apparatus for fish toxicology studies. Water Res. 1: 21–29.

Ontario. The Environmental Protection Act. 1971. Chapter 86, as amended by Chapter 1, s. 69; 1972, Chapter 106; 1973, Chapter 94; 1974, and Chapter 20; Dec. 1974. 54 p.

Seppovaara, O., and P. Hynninen. 1970. On the toxicity of sulfate mill condensate. Pap. Puu-Papper Och Trä 52: 11–23.

Shumway, D. L. 1968. The effects of unbleached kraft mill effluents on salmon. II. Flavor of jack coho salmon. Natl. Coun. Air Stream Improv. Inc., New York, N.Y. Tech. Bull. 217: 47–53.

Sprague, J. B., and D. W. McLeese. 1968. Toxicity of kraft pulp mill effluents for adult and larval lobsters, and juvenile salmon. Water Res. 2: 753–760.

Swabey, Y. H. 1964. A study of the flavor of fishes from Lake St. Lawrence, St. Lawrence River, and Lake St. Francis. Ont. Water Resour. Comm. Rep. 24 p.

Thaysen, A. C., and F. T. K. Pentelow. 1936. The origin of an earthy or muddy taint in fish. II. The effect on fish of the taint produced by an odoriferous species of Actinomycetes. Ann. Appl. Biol. 23: 105–109.

Tokar, E. M., and E. L. Owens. 1968. The effects of unbleached kraft pulp mill effluents on salmon. I. Growth, food consumption and swimming ability of juvenile chinook salmon. Natl. Coun. Air Stream Improv. Inc., New York, N.Y. Tech. Bull. 217.

Warren, C. E., and G. E. Davis. 1967. Laboratory studies on the feeding, bioenergetics and growth of fish, p. 175–214. *In* S. D. Gerking [ed.] The biological basis for freshwater fish populations. Blackwell Scientific Publications, Oxford and Edinburgh.

Warren, C. E., et al. 1973. Effects of kraft effluent on the growth and production of salmonid fish. Tappi 57: 127–132.

Webb, P. W., and J. R. Brett. 1972. The effects of sublethal concentrations of whole bleached kraft mill effluent on the growth and food conversion efficiency of underyearling sockeye salmon. J. Fish. Res. Board Can. 29: 1555–1563.

Wells, D. L. 1970. Flavor evaluation of whitefish from Thunder Bay and Grand Portage Bay. Ont. Water Resour. Comm. Rep. 8 p.

1972. Rubber manufacturing wastes and their effects on fish and water quality. Ont. Minist. Environ. Toronto, Ont. 60 p.

Werner, A. E. 1963. Sulphur compounds in kraft mill effluents. Can. Pulp and Pap. Ind. 16(3): 35–43.

Density, Distribution, and Movement of Nipigon Bay Fishes in Relation to a Pulp and Paper Mill Effluent[1]

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Density of pelagic fish in accessible portions of Nipigon Bay was lower offshore, less than 100 fish/10,000 m^3, and greater nearshore, less than 1800 fish/10,000 m^3. Conditions at Red Rock caused intense aggregation there and caused species dominance to shift to sucker at the mill discharge from yellow perch elsewhere. Plume shape and direction did not alter the localized pattern of distribution. Two typical responses to plume concentrations were found using suckers fitted with ultrasonic transmitters. Fish released in high discharge concentrations (>15% dilution by volume) became disoriented for as much as several hours, then appeared to search for "background" conditions. Fish released in low discharge concentrations (<15%) immediately initiated an avoidance reaction. Although individuals tended to avoid areas of altered water quality, the community aggregated at Red Rock in response to, perhaps, increased production of benthic macroinvertebrates. However, telemetry indicated that residence time was short in the area of altered water quality.

KELSO, J. R. M. 1977. Density, distribution, and movement of Nipigon Bay fishes in relation to a pulp and paper mill effluent. J. Fish. Res. Board Can. 34: 879–885.

La densité des poissons pélagiques dans les portions accessibles de la baie Nipigon est plus faible au large, moins de 100 poissons/10 000 m^3, et plus forte près du rivage, moins de 1 800 poissons/10 000 m^3. Par suite des conditions qui prévalent à Red Rock, il y a intense agrégation à cet endroit, et la dominance des espèces se déplace vers les catostomes à l'émissaire du moulin, alors que la perchaude est dominante ailleurs. La forme et la direction de la couche superficielle ne modifient pas la configuration localisée de la distribution. Nous avons observé deux réponses typiques aux concentrations de la couche superficielle chez des catostomes munis de transmetteurs ultrasonores. Les poissons relâchés dans de hautes concentrations d'effluent (dilution >15% en volume) sont désorientés pendant plusieurs heures et semblent ensuite rechercher des conditions d'« arrière-plan ». Les poissons relâchés dans de faibles concentrations d'effluent (<15%) ont une réaction immédiate d'évitement. Bien que les individus aient tendance à éviter les régions où la qualité de l'eau est altérée, la communauté se rassemble à Red Rock peut-être en réponse à une production accrue de macroinvertébrés benthiques. Cependant, la télémétrie indique que la résidence dans la région où la qualité de l'eau est altérée est de courte durée.

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EFFECTS of pulp and paper mill wastewaters can be multifold. For example, fish communities are affected by suspended solids (Sprague and McLeese 1968), oxygen depletion from increased biochemical oxygen demand (reviewed in NAS/NAE 1974), toxic wastes (Marier 1973) and taste and odor creating substances (Shumway and Palensky 1973). Only limited information exists on behavioral response of aquatic organisms to administered quantities of whole pulp mill wastes or their constituents. Also, environmental studies have basically only collected and enumerated samples under suspected differing levels of influence.

Reliable observations of community response

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[1] This paper is part of a series concerning the impact of pulp and paper mill wastewater discharges into Lake Superior. This study was carried out in 1974 and 1975 under the auspices of the International Joint Commission, Upper Great Lakes Reference Group.

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or individual reaction to environmental perturbation are rare, yet they are essential to understanding natural community response. This study sought to provide an overview of the fish community's density and distribution in relation to conditions caused by the pulp and paper mill discharge. Furthermore, to better understand the observed alterations in community structure, individual reaction to the effluent was investigated by limited use of ultrasonic telemetry.

Methods

FISH ABUNDANCE AND DISTRIBUTION

Fish abundance and distribution was assessed through the use of electro-acoustic techniques designed for fish detection. Details of equipment and test results are presented elsewhere (Kelso et al. 1974; Kelso and Minns 1975; White 1975). Basically, the system consisted of an 80 kHz EDO Western transceiver having a 100 μs pulse length and transmission rate of 4 Hz. Time varied gain (TVG) characteristics are described by White (1975). An echo analysis and control subsystem (EACS) provided supervisory control functions to operate the data acquisition, storage, display (a fiber optic cathode ray tube recorder, Honeywell, which uses photosensitive recording paper), and data logging (a Hewlett Packard mechanical digital printer) features. The EACS accepted received echoes from the receiver, applied amplitude and depth sorting and accumulated digital counts over a number of successive transmissions corresponding to four amplitude ranges for each of six selectable depth ranges. Incoming signals from the receiver were envelope detected by the EACS, compared to five reference voltages, and timed from the time the detected signal exceeded the lowest reference voltage threshold, and the appropriate "word" in the logic memory was incremented. Amplitude sorting occurred in each of six variable depth ranges commencing 3 m below the transducer face. Echo sizing capabilities exist, but all data above the threshold (corresponding to fish size of 6 cm on the acoustic axis) were grouped. To eliminate counting of bottom echoes, the bottom signal which exceeded the fifth and highest amplitude threshold terminated echo processing for that transmission even though depth dates could be set to receive below the actual bottom. Consequently, fish detection within one pulse length (approximately 15 cm) of the bottom was precluded. Further aspects of the bottom lock, performance and engineering specifications of the components and system performance are provided by White (1975).

Instrumentation was mounted in a 14 m launch with the transducer situated to the rear of the vessel on the port side. The transducer, housed in a streamlined pod, had a fared support projecting upward to enable over-the-side mounting and to decrease turbulent interference at the transducer face.

Cruise patterns to relate fish distribution and abundance to water quality were identical to those used for synoptic plume sampling (Minns 1977). In the Nipigon Bay census, zigzag cruise lines were run from the mouth of the Nipigon River to within 5 km of the eastern end of Ile la Grange. Data were summed over 360 transmissions in censuses in the Red Rock area and over 720 transmissions in the survey of Nipigon Bay. Depth gates were similar for both censuses (3–6, 6–9, 9–12, 12–15, 15–18, and 18–25 m).

Data treatment was essentially similar to that used by Kelso et al. (1974) and Kelso and Minns (1975) except that a computer was used to analyze all data.

Equipment and techniques for monitoring water quality, methods of data reduction and aspects of Nipigon Bay water quality used herein were taken from Minns (1977). Conductivity was used to indicate area influenced by the discharge on any day of study.

FISH MOVEMENT

Telemetry apparatus, tracking procedures and data treatment for monitoring ultrasonic tagged fish are available elsewhere (Kelso 1976) and only a brief description follows. Temperature-sensing ultrasonic transmitters 1.3 by 3.0 cm and weighing 4.7 g in water were attached externally to white sucker, *Catostomus commersoni*, the dominant species of fish near the effluent. A Bayshore Systems Corp. model RT-22 pulse rate to temperature converter/decoder was used in conjunction with a Smith Root receiver. Pulse rate, a function of temperature, was recorded as mv on a strip chart recorder. Since reliability of transmitters decayed rapidly after 24 h and reaction on encountering the effluent was of interest, tracks were terminated once tagged fish left the area of influence.

Experimental fish were captured by hoop net approximately 3 km south of the discharge and held in artificially aerated lake water in the tracking boat prior to tagging and release. Captures were assumed to be made beyond the influence of the discharge. Tracking was done only during daylight as numerous obstacles in the water made nighttime tracking difficult and dangerous. Also, water quality surveillance was performed only during daylight.

Results and Discussion

FISH DENSITY AND DISTRIBUTION — NIPIGON BAY

Depths of less than 3 m prevented access of the vessel to approximately 50% of Nipigon Bay (Fig. 1). Density of pelagic fish in the accessible northern channel of Nipigon Bay was found to be least, 0 to 100 fish/10,000 m^3 offshore in the 3–6 m depth shell and greatest, up to 1800/10,000 m^3, nearshore. Distribution tended to be patchy (Fig. 1), particularly nearshore, but low densities were always apparent in the open waters. Although not readily apparent from Fig. 1, densities were low near rock faces of the shoreline where depth increased sharply, e.g. near Vert

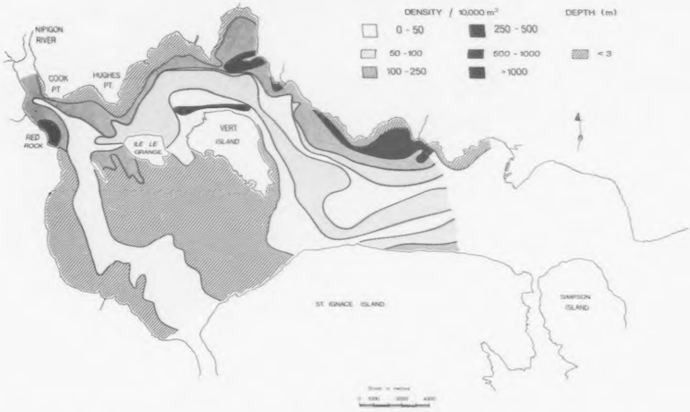


FIG. 1. Abundance and distribution of fish, between 3 and 6 m, in accessible regions of Nipigon Bay, Lake Superior.

Island and Ile la Grange. The northern shore generally tended to support high densities of fish and abundance was greatest near promontories which sharply projected into the bay.

Greatest density in the 3–6 m shell was found, however, near the town of Red Rock (Fig. 1) where abundance was between 400 and 2000/ 10,000 m³ within 1 km of the discharge.

In the six depth shells monitored, density was greatest in the uppermost strata and decreased regularly with depth.

Depth shell (m)	Range in density per 10,000 m³	Mean density per 10,000 m³
3–6	0.0–1834.7	167.4
6–9	0.0–661.1	18.3
9–12	0.0–311.1	8.5
12–15	0.0–294.5	8.3
15–18	0.0–177.4	8.3
18–25	0.0–30.3	4.1

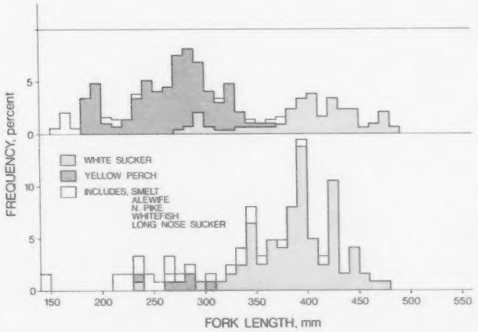


FIG. 2. Size frequency distribution of major fish species in experimental gillnet catches at Red Rock (*lower*) and uninfluenced (*upper*) sites.

Instances of 0 fish in 720 transmissions (3 min of observation) were found at all four depths. The upper ranges in density (text table) for the four upper depth shells (3–15 m) were encountered in observations made near Red Rock.

Species composition of net catches varied considerably in Nipigon Bay.

Species	Percent Composition: Red Rock	Percent Composition: Nipigon Bay
White sucker (*Catostomus commersoni*)	73.2	33.6
Longnose sucker (*C. catostomus*)	18.7	1.0
Yellow perch *Perca flavescens*	4.9	59.9
Smelt (*Osmerus mordax*)	1.6	3.4
Alewife (*Alosa pseudoharengus*)	1.6	1.4
Northern pike (*Esox lucius*)	—	0.3
Whitefish (*Coregonus clupeaformis*)	—	0.3

White and longnose suckers dominated catches near Red Rock while yellow perch followed by white suckers dominated catches made at uninfluenced sites in Nipigon Bay. Smelt and alewife were in similar numbers at influenced and uninfluenced sites. Net catches, although not reflecting species composition of offshore pelagic fish (where density was least), likely adequately reflected species found in nearshore areas (where density was greatest) and consequently areas where water quality alterations were greatest.

Analysis of the gillnet catches by length (Fig. 2) reflected the differences in species composition and subsequently fish size in the community. Suckers contributed most to formation of the larger size fraction of catches, from 300 to 490 m. Change in species composition caused the shift in dominance of size frequency distributions (Fig. 2).

FISH DENSITY AND DISTRIBUTION — RED ROCK

Distribution and density of the Nipigon Bay fish community was apparently altered by the discharge from the pulp and paper mill at Red Rock (Fig. 1). Sampling near Red Rock was accordingly intensified and related to localized changes in water quality. Only three typical patterns of plume dispersion, as measured by conductivity (Fig. 3), were apparent during the eleven censuses conducted.

Plumes were found to emanate south (Fig. 3a), north (Fig. 3b), and offshore (Fig. 3c) from the point of discharge. See Minns (1977) for further detail of plume behavior. In all instances, fish density was greatest adjacent to the point of entry and decreased with increasing distance from shore. Abundance of pelagic fish decreased with increasing depth but since water quality was most affected in surface waters, analysis of acoustic data was confined to the 3–6 m depth shell (Fig. 3). As in the Nipigon Bay census, density was lowest in the deeper waters offshore (Fig. 3). By regression analysis, it was found that abundance was related to distance from shore:

Date	Plume direction	Intercept	Slope	Correlation coefficient	*F* Regr.
July 18	south	2777	−7038	0.765	66.42
July 22	north	2073	−4419	0.636	40.76
July 29	offshore	1495	−2282	0.553	28.24

Abundance, taken as the mean of all samples in 3–6 m, varied among plume directions. The south plume had 1971 fish/10,000 m^3, the north plume 2005/10,000 m^3, and the offshore plume 1214/10,000 m^3. However, fish distribution changed very little (Fig. 3). Fish were always most abundant in a band along shore extending from the wharf south to Five Mile Point. Maximum densities, up to 20,000 fish/10,000 m^3 were found adjacent to the input from the Domtar mill.

Gillnet sets (text table) indicated that suckers were dominant at Red Rock, forming 91.9% of total catch. Longnose sucker accounted for almost 20% of the population there, although it was a minor contributor to Nipigon Bay catches (Fig. 2). Conversely, yellow perch, a major component of the Nipigon Bay community, was rare in areas maximally influenced by the discharge.

Conditions at Red Rock markedly altered distribution of the Nipigon Bay fish community by causing intense aggregation in the vicinity of the pulp and paper mill discharge. From limited net catches, species composition was altered (Fig. 2 and text table) from that in uninfluenced areas of Nipigon Bay. Few other investigations support these observations and conclusions. An early environmental study (Dymond and Delaporte 1952) indicated that fish community structure was altered by pulp and paper mill in the Spanish River, Ont., in that white sucker dominated the community in influenced areas concomitant with the loss in other species.

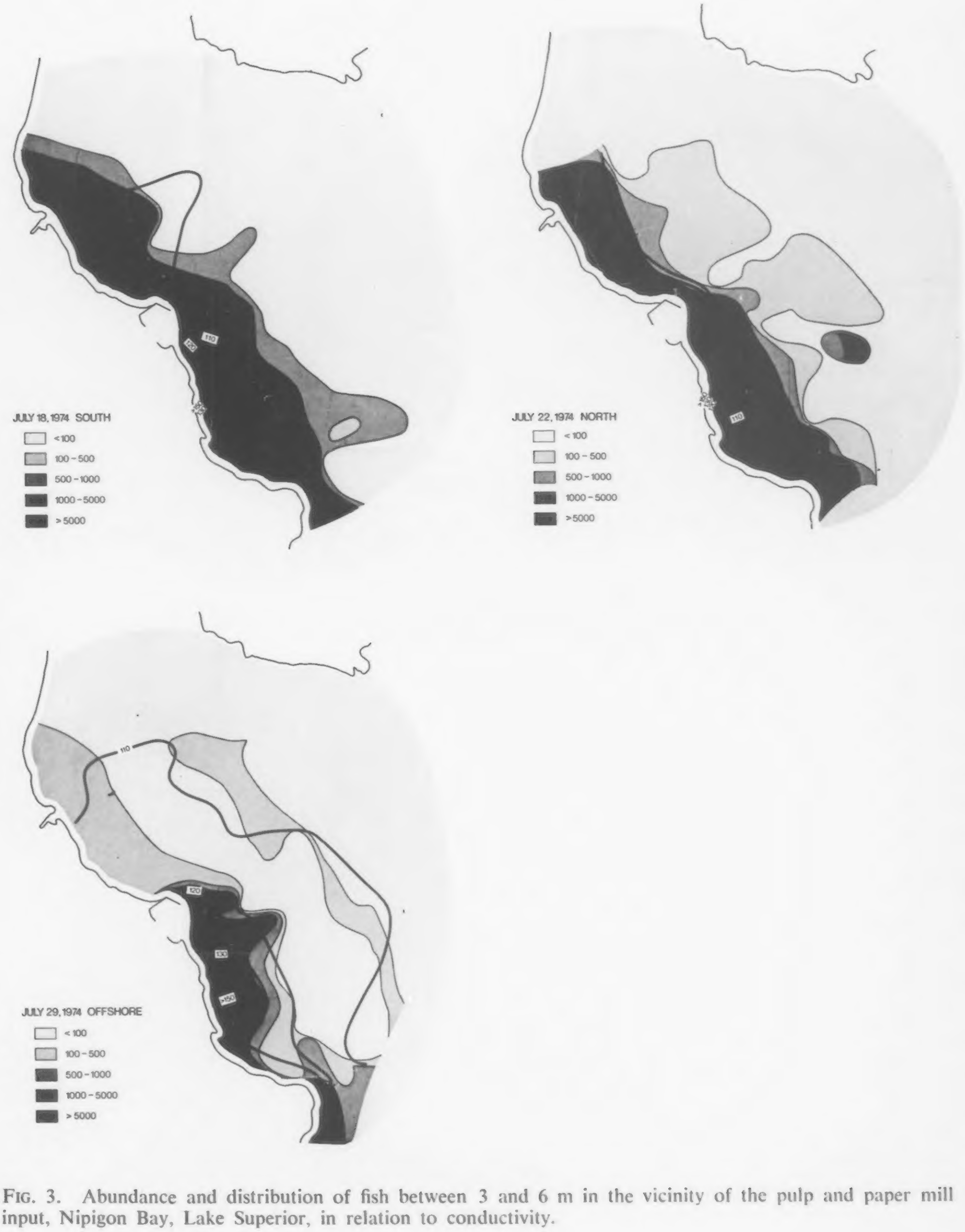
INDIVIDUAL RESPONSE TO THE PLUME

Between July 23 and August 6, 1974, eight white sucker carrying ultrasonic temperature-sensing transmitters were released and tracked in the Red Rock area for a total of 44 h (Table 1). Tracks were generally from 6 to 8 h in duration. The two tracks less than 6 h resulted from inclement weather.

Four white sucker were released in each of high (>15%) and low (<15%) discharge concentrations (Table 1) and two types of responses were evident (Fig. 4). Those released at low concentrations showed pronounced local movement in and out of higher concentrations (Fig. 5) as reflected by temperature (wastewater temperatures were up to 15°C above ambient). Thereafter, fish appeared to zigzag in and out of higher nearshore concentrations (reflected by sharp turns (Table 1) and Fig. 4 and 5) while progressing in a general southerly direction.

Fish released at higher concentrations showed localized bursts of movements lasting up to 6 h (Table 1). Temperature data (Fig. 5) obtained from transmitters indicated that although low concentrations were encountered during the high activity period, these lower effluent concentrations did not appear to influence movement. Movements of fish released in high concentrations were sporadic and irregular during early parts of the track and became less erratic after up to 4 h (Fig. 4 and 5). Later portions of these tracks approximated movements of fish released into lower concentrations.

Telemetry indicated an avoidance reaction by white sucker to the discharge and seems contradictory to high estimates of density and intense localized distribution. However, it is likely that through telemetry, only response to discharge concentration was reflected. Avoidance of low concentrations of pulp mill effluent has been detected elsewhere (Jones et al. 1956; Sprague 1968; Elson et al. 1974) and confirms the present telemetry


110
120
JULY 18, 1974 SOUTH
<100
100 - 500
500 - 1000
1000 - 5000
>5000
110
JULY 22, 1974 NORTH
<100
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500 - 1000
1000 - 5000
>5000
110
120
130
>150
JULY 29, 1974 OFFSHORE
<100
100 - 500
500 - 1000
1000 - 5000
>5000

FIG. 3. Abundance and distribution of fish between 3 and 6 m in the vicinity of the pulp and paper mill input, Nipigon Bay, Lake Superior, in relation to conductivity.

TABLE 1. Data for eight tracks of white sucker released at high (> 15%) and low (< 15% dilution by volume) relative concentrations, 1974.

Date 1974	Release conc.	Standard length (*mm*)	Time followed (*min*)	Distance travelled (*m*)	No. of turns	Average angle of turn	Average speed (total track) (*cm/s*)	Comments
July 23	low	427	351	2450	17	89	11.63	most position changes associated with "avoidance" of plume in early part of track
July 25	high	373	380	678	17	128	2.97	
July 27	low	341	350	1812	19	87	8.86	
July 29	high	406	224	1070	17	117	7.96	
July 30	high	365	196	1030	17	114	2.42	
August 1	low	440	429	955	21	79	3.71	
August 3	high	443	368	260	16	134	1.18	
August 6	low	351	331	610	21	70	3.07	temperature decoder fault

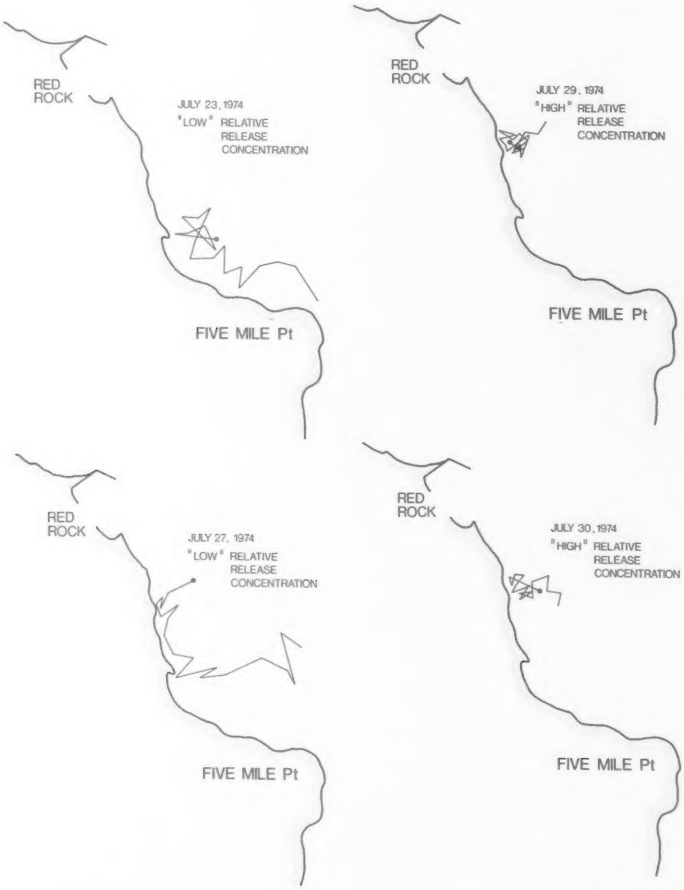
RED ROCK
JULY 23, 1974
"LOW" RELATIVE RELEASE CONCENTRATION
FIVE MILE Pt
RED ROCK
JULY 29, 1974
"HIGH" RELATIVE RELEASE CONCENTRATION
FIVE MILE Pt
RED ROCK
JULY 27, 1974
"LOW" RELATIVE RELEASE CONCENTRATION
FIVE MILE Pt
RED ROCK
JULY 30, 1974
"HIGH" RELATIVE RELEASE CONCENTRATION
FIVE MILE Pt

FIG. 4. Tracks of four white sucker released in high and low relative discharge concentrations.

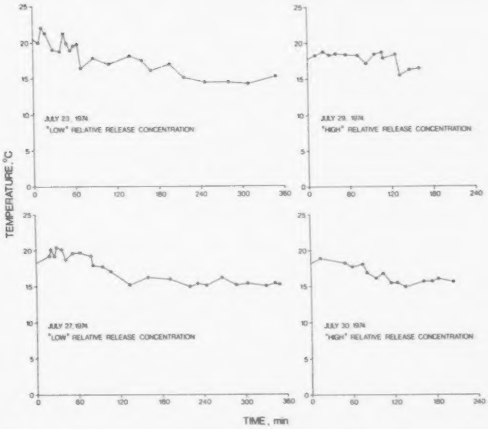

FIG. 5. External temperature of white sucker (reflects relative discharge concentration) released in high and low relative discharge concentrations.

studies. However, since benthic invertebrates tend to be extremely abundant beyond the immediate outfall, although limited in species (Beak 1971; VanderWal 1977), it seems likely that for certain species the feeding response to high benthic biomass overrides the avoidance reaction to the effluent. The observed changes in the fish community of Nipigon Bay therefore likely result not only from the short-term response of fish to the effluent, but also the long-term alteration in environment, both acting in concert.

BEAK, T. W. 1971. Biological survey of Nipigon Bay — 1970. Consult. Rep. 13 p.

DYMOND, J. R., AND A. V. DELAPORTE. 1952. Pollution of the Spanish River. Ont. Dept. Lands For. Tech. Rep. 106 p.

ELSON, P. F., L. N. LAUZIER, AND V. ZITKO. 1974. A preliminary study of salmon movements in a polluted estuary, p. 325–330. *In* M. Ruivo [ed.] Marine pollution and sea life. Fishing News (Books) Ltd., London.

JONES, B. F., C. E. WARREN, C. E. BOND, AND P. DOUDOROFF. 1956. Avoidance reactions of salmonid fishes to pulp mill effluents. Sewage Ind. Wastes 28: 1403–1413.

KELSO, J. R. M. 1976. Response of yellow perch (*Perca flavescens*) and white sucker (*Catostomus commersoni*) to thermal effluents in a nearshore Great Lakes habitat. J. Fish. Res. Board Can. 33: 42–53.

KELSO, J. R. M., AND C. K. MINNS. 1975. Summer distribution of the nearshore fish community near a thermal generating station as determined by acoustic census. J. Fish. Res. Board Can. 32: 1409–1418.

KELSO, J. R. M., R. G. DOWD, AND E. E. PICKETT. 1974. A digital echo-counting system used in determining abundance of freshwater pelagic fish in relation to depth. J. Fish. Res. Board Can. 31: 1101–1104.

MARIER, J. R. 1973. The effects of pulp and paper wastes on aquatic life with particular attention to fish and bioassay procedures for assessment of harmful effects. NRC (Nat. Res. Counc. Can.) publ. BY 73-3 (ES): 33 p.

MINNS, C. K. 1977. Analysis of a pulp and paper mill effluent plume. Fish. Res. Board Can. 34. (This issue)

NATIONAL ACADEMY OF SCIENCES/NATIONAL ACADEMY OF ENGINEERING. 1972. Water quality criteria 1972. Environ. Study Board, NAS/NAE 594 p.

SHUMWAY, D. L., AND J. R. PALENSKY. 1973. Impairment of the flavor of fish by water pollutants. U.S. Environ. Prot. Agency Rep. EPA-R3-73-010.

SPRAGUE, J. B. 1968. Avoidance reactions of salmonid fish to representative pollutants. Water Res. 2: 23–24.

SPRAGUE, J. B., AND D. W. MCLEESE. 1968. Different toxic mechanisms in Kraft pulp mill effluent for two aquatic animals. Water Res. 2: 761–765.

VANDER WAL, J. 1977. Relation between Nipigon Bay benthic macroinvertebrates and selected aspects of their habitat. J. Fish. Res. Board Can. 34. (This issue)

WHITE, B. F. 1975. An inland waters acoustic echo amplitude/depth analysis system for monitoring fish population distributions. Can. Cent. Inland Waters. (Unpublished rep.)

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